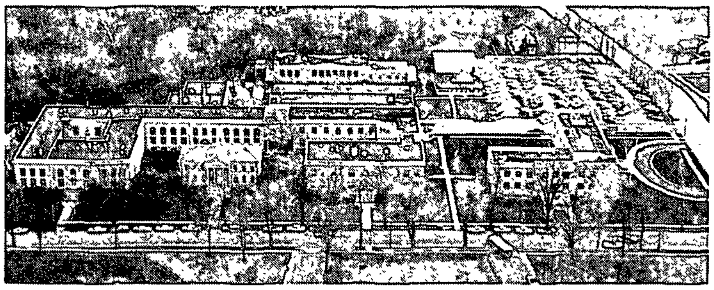

THE INSTITUTE OF PAPER CHEMISTRY, APPLETON, WISCONSIN

PULPING PROCESSES

PROJECT ADVISORY COMMITTEE MEETING

MARCH 24-25, 1987

HANDOUT

NOTICE & DISCLAIMER

TABLE OF CONTENTS

Research Overview

E. W. Malcolm

CHEMICAL SCIENCES DIVISION

STAFF (MARCH 1987)

9 PH.D. (FACULTY)

22 B.S./M.S.

RESEARCH AREAS

CHEMICAL PULP

KRAFT CHEMICAL RECOVERY

HIGH YIELD PULPS

RESEARCH TYPE

IPC FUNDED

IPC STUDENT

CONTRACT

IPC RESEARCH BUDGETS (1986-1987) - CHEMICAL SCIENCES DIVISION ($1000)

IPC FUNDED

CHEMICAL PULPING	
3288 - FINE STRUCTURE OF WOOD PULP FIBERS	75
3475 - FUNDAMENTALS OF SELECTIVITY IN PULPING AND BLEACHING	150
3474 - IMPROVED PROCESSES FOR BLEACHED PULP	35
3477*- DEVELOPMENT AND APPLICATION OF ANALYTICAL TECHNIQUES	13
	273
RECOVERY	
3473-1-FUNDAMENTAL PROCESSES IN ALKALI RECOVERY FURNACES	230
3456-2-SMELT-WATER EXPLOSIONS	20
3477* -DEVELOPMENT AND APPLICATION OF ANALYTICAL TECHNIQUES	13
3605 -COMPUTER MODEL OF RECOVERY FURNACE	20
	283
HIGH YIELD PULPING	
3566 - SEPARATION OF STRONG, INTACT FIBERS	175
3524 - FUNDAMENTALS OF BRIGHTNESS STABILITY	140
3521-2-RAMAN MICROPROBE INVESTIGATION OF MOLECULAR STRUCTURE AND ORGANIZATION IN THE NATIVE STATE OF WOODY TISSUE	45
3477*- DEVELOPMENT AND APPLICATION OF ANALYTICAL TECHNIQUES	13
	373
OTHER	
3534 - EXPLORATORY RESEARCH	60
3477*- ANALYTICAL (PAPER)	26
	86
TOTAL IPC FUNDED	929

CONTRACT RESEARCH

GOVERNMENT FUNDED		
3473-6-FUNDAMENTAL STUDIES OF BLACK LIQUOR COMBUSTION		
	IPC	220
	NBS	205
3521-3-RAMAN MICROPROBE INVESTIGATION OF MOLECULAR STRUCTURE AND ORGANIZATION IN THE NATIVE STATE OF WOODY TISSUE		50
NEW RAMAN MICROPROBE		100
		575
NONGOVERNMENT FUNDED		
RIVER SURVEY		210
OTHER		122
		332
	TOTAL CONTRACT RESEARCH	907
TOTAL FUNDED AND CONTRACT		1,836

(49% CONTRACT)
(51% CONTRACT)

IPC STUDENT RESEARCH

	PH.D.	M.S.
CHEMICAL PULPING	8	5
KRAFT CHEMICAL RECOVERY	10	4
HIGH YIELD PULP	2	1
	20	10

IPC RESEARCH BUDGETS (1986-1987) - CHEMICAL SCIENCES DIVISION ($1000)

CONTRACT RESEARCH		
GOVERNMENT FUNDED		
3473-6-FUNDAMENTAL STUDIES OF BLACK LIQUOR COMBUSTION	IPC	220
	NBS	205
3521-3-RAMAN MICROPROBE INVESTIGATION OF MOLECULAR STRUCTURE AND ORGANIZATION IN THE NATIVE STATE OF WOODY TISSUE		50
NEW RAMAN MICROPROBE		100
		575
NONGOVERNMENT FUNDED		
RIVER SURVEY		210
OTHER		122
		332
TOTAL CONTRACT RESEARCH		907

IPC RESEARCH BUDGETS (1986-1987) - CHEMICAL SCIENCES DIVISION ($1000)

IPC FUNDED

Chemical Pulping	273
Recovery	283
High Yield Pulping	373
Other	86
TOTAL IPC FUNDED	929

IPC RESEARCH BUDGETS (1986-1987) - CHEMICAL SCIENCES DIVISION ($1000)

IPC FUNDED

Chemical Pulping

3288 - Fine Structure of Wood Pulp Fibers	75
3475 - Fundamentals of Selectivity in Pulping and Bleaching	150
3474 - Improved Processes for Bleached Pulp	35
3477*- Development and Application of Analytical Techniques	13
	273

IPC RESEARCH BUDGETS (1986-1987) - CHEMICAL SCIENCES DIVISION ($1000)

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	373

IPC RESEARCH BUDGETS (1986-1987) - CHEMICAL SCIENCES DIVISION ($1000)

IPC FUNDED

OTHER

3534 - EXPLORATORY RESEARCH	60
3477*- ANALYTICAL (PAPER)	26
	96

Project 3473-1

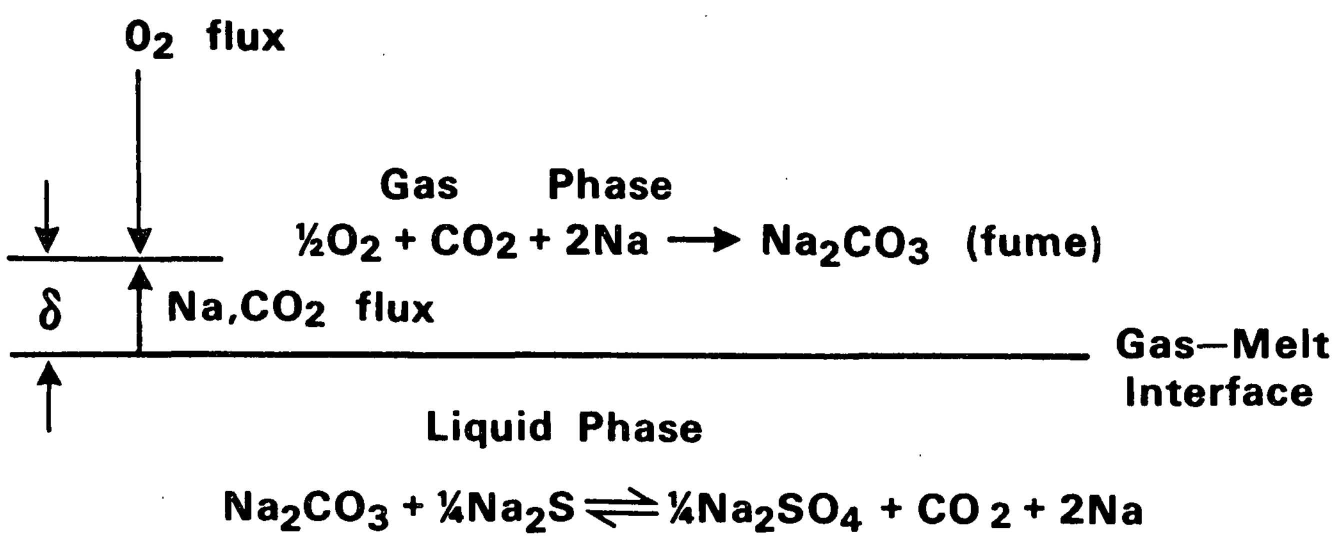
John Cameron

Dave Clay

Mark Robinson

Kathy Crane

FUME GENERATION



FUME GENERATION UNDER OXIDIZING CONDITIONS

Typical Fume Generation Rates during Sulfide Oxidation

Initial Melt Composition

Na_2CO_3 = .77 mole
Na_2S = .06 mole

Purge = 1.15 L/min at 13.0% O_2
Temperature = 954°C

Calculated Concentrations

Time, s	Na_2SO_4, mole/L	Na_2S, mole/L	Fume Generation Rate, g/min	Fume/Off-Gas Mole Na_2CO_3/ Mole N_2
191	0.010	0.049	0.0212	0.0043
278	0.015	0.044	0.0212	0.0043
452	0.025	0.035	0.0225	0.0046
627	0.035	0.025	0.0239	0.0049
738	0.041	0.019	0.0245	0.0050
933	0.052	0.008	0.0241	0.0049

Fume Generation with Carbon Monoxide

$$CO + Na_2CO_3 \text{ ----> } 2\ CO_2 + 2\ Na(g) \quad (1)$$

Initial Melt Composition

Na_2CO_3 = 0.77 mole
Na_2S = 0.03 mole
Na_2SO_4 = 0.0 to 0.02 mole

N_2 Purge = 1.0 L/min
CO = 0.0 to 0.1 L/min

Temperature = 954°C

Na_2SO_4 added, mole	Purge Rate N_2, L/min	Purge Rate CO, L/min	Fume Generation Rate, g/min	Fume/N_2 Mole Na_2CO_3/Mole N_2
0.0	1.0	0.0	0.00076	0.00016
0.0	0.98	0.01	0.00036	0.00008
0.0	0.98	0.03	0.00076	0.00016
0.0	0.98	0.05	0.0008	0.00017
0.0	0.98	0.1	0.00072	0.00015
0.01	0.98	0.1	0.0	0.0
0.02	0.98	0.1	0.00016	0.00003

Fume Generation in the Presence of Carbon

$$2\ C + Na_2CO_3 \longrightarrow 3\ CO + 2\ Na(v) \qquad (4)$$

Initial Melt Composition

Na_2CO_3 = 0.77 mole
Na_2S = 0.03 mole

Purge

N_2 = 1.0 L/min

Temperature = 954°C

Carbon added, mole	Purge Rate N_2, L/min	Fume Generation Rate, g/min	Fume/N_2 Mole Na_2CO_3/ Mole N_2
0.016, S	1.0	0.0012	0.00025
0.032, S	1.0	0.0039	0.00082
0.016, K	1.0	0.002	0.00042
0.032, K	1.0	0.0025	0.00053

S = Soda Char, K = Kraft Char

The Effect of Hydrogen on Fume Generation

$$H_2 + Na_2CO_3 \text{ ----> } H_2O + CO_2 + 2\ Na(v) \qquad (2)$$

$$H_2 + Na_2CO_3 \text{ ----> } 2\ NaOH + CO \qquad (3)$$

Initial Melt Composition

Na_2CO_3 = 0.77 mole
Na_2S = 0.03 mole
Na_2SO_4 = 0.0 to 0.03

Purge

N_2 = 1.0 L/min
H_2 = 0.0 to 0.1 L/min

Temperature = 954°C

Na_2SO_4 added, mole	Purge Rate N_2, L/min	Purge Rate H_2, L/min	Fume Generation Rate, g/min	Fume/N_2 Mole Na_2CO_3/ Mole N_2
0.0	1.0	0.0	0.00076	0.00016
0.0	0.92	0.02	0.0007	0.00016
0.0	0.92	0.05	0.0008	0.00018
0.0	0.92	0.1	0.002	0.00046
0.03	0.92	0.1	0.002	0.00046

Effect of Sodium Hydroxide on Fume Generation

Melt Composition

Na_2CO_3 = 0.77 mole
Na_2S = 0.0 to 0.03 mole
NaOH = 0.0 to 0.1 mole

Purge

N_2 = 1.0 L/min

Temperature = 954°C

Na_2S Added, mole	NaOH Added, mole	Fume Generation Rate, g/min	Fume/Off-Gas mole Na_2CO_3/ mole N_2
0.0	0.012	0.0	0.0
0.0	0.031	0.0	0.0
0.03	0.0	0.00076	0.00016
0.03	0.01	0.0007	0.00015
0.03	0.10	0.0007	0.00016

Potassium Behavior during Fume Generation under Oxidizing Conditions

Temperature = 954°C
O_2 Flow Rate = 0.021 L/min
N_2 Flow Rate = 1.0 L/min

Initial Melt Composition				Fume Generation, g/min	Fume K/Na Molar Ratio	Enrichment Factor
Na_2CO_3, mole	K_2CO_3, mole	Na_2S, mole	K/Na Molar Ratio			
0.75	0.02	0.03	0.0256	0.075	0.0225	0.88
0.71	0.06	0.03	0.0811	0.0765	0.0888	1.09
0.67	0.1	0.03	0.143	0.0683	0.141	0.99
0.37	0.4	0.03	1.0	0.058	0.96	0.96
0.1	0.71	0.03	5.46	0.053	6.01	1.10

Chloride Enrichment from Carbonate Melts

Melt Composition

Na_2CO_3 = 0.575 to 0.62 mole
Na_2S = 0.143 to 0.16 mole
NaCl = 0.10 to 0.20 mole

Purge Rate

N_2 = 1.0 L/min
O_2 = 0.0 to 0.1 L/min

Temperature = 954 to 982°C

Run No.	Temp., °C	Melt Cl/Na Molar Ratio	O_2 Flow Rate, L/min	Fume Cl/Na Molar Ratio	Enrichment Factor
326	954	0.10	0.0	0.86	8.6
327	954	0.049	0.1	0.0815	1.66
328	982	0.049	0.1	0.0759	1.55
329	954	0.122	0.1	0.221	1.81
330	982	0.122	0.1	0.175	1.43

$$p_{NaCl}(T) = p^*_{NaCl}(T)\ X_{NaCl}$$

Here, $P_{NaCl}(T)$ is the equilibrium partial pressure of NaCl at temperature T; p^*_{NaCl} is the vapor pressure of pure NaCl at temperature T; and X_{NaCl} is the mole fraction of NaCl in the melt.

Calculated and Measured Vaporization Rates of Sodium Chloride during Sulfide Oxidation in a Carbonate Melt

Run No.	Total Fume Generation, g/min	Cl Content of Fume wt. %	Calculated NaCl Vaporization, g/min	Measured NaCl Vaporization, g/min
327	0.0146	5.34	0.0012	0.00128
328	0.0193	4.95	0.00217	0.00158
329	0.0162	14.1	0.0031	0.00376
330	0.02485	11.5	0.00462	0.00471

Effect of Chloride on Potassium Enrichment during Sulfide Oxidation

Melt Composition

Na_2CO_3 = 0.565 mole
Na_2S = 0.14 mole
NaCl = 0.1 to 0.16 mole
KCl = 0.02 to 0.10 mole

Purge Rate

N_2 = 1.0 L/min
O_2 = 0.0 to 0.1 L/min

Temperature = 954°C

Run No.	Melt Cl/(Na+K)	Melt K/(Na+K)	O_2 Flow Rate L/min	Fume Cl/(Na+K)	Fume K/(Na+K)	Enrichment Factor Cl	Enrichment Factor K
343	0.119	0.0187	0.0	0.745	0.119	6.3	6.8
331	0.122	0.062	0.1	0.164	0.10	1.3	1.6
344	0.119	0.0188	0.1	0.173	0.046	1.5	2.4
345	0.127	0.0278	0.1	0.16	0.051	1.3	1.9
346	0.116	0.0129	0.1	0.19	0.026	1.5	2.0

Potassium and Chloride Enrichment Factors

Run No.	Calculated Enrichment Factors Cl	Calculated Enrichment Factors K	Observed Enrichment Factors Cl	Observed Enrichment Factors K
331	1.6	1.2	1.3	1.6
344	1.3	1.2	1.5	2.4
345	1.3	1.2	1.3	1.9
346	1.3	1.2	1.5	2.0

Conclusions:

1) Oxidation enhanced vaporization is a major source of fume in the kraft furnace.

2) Sodium Hydroxide is not highly volatile.

3) Lower than equilibrium predicted K and Cl enrichment factors result from dilution from oxidation enhanced vaporization.

4) Sodium chloride vaporization can be described assuming Raoult's Law holds.

Kristin Ann Goerg, Ph.D.

A STUDY OF FUME PARTICLE DEPOSITION

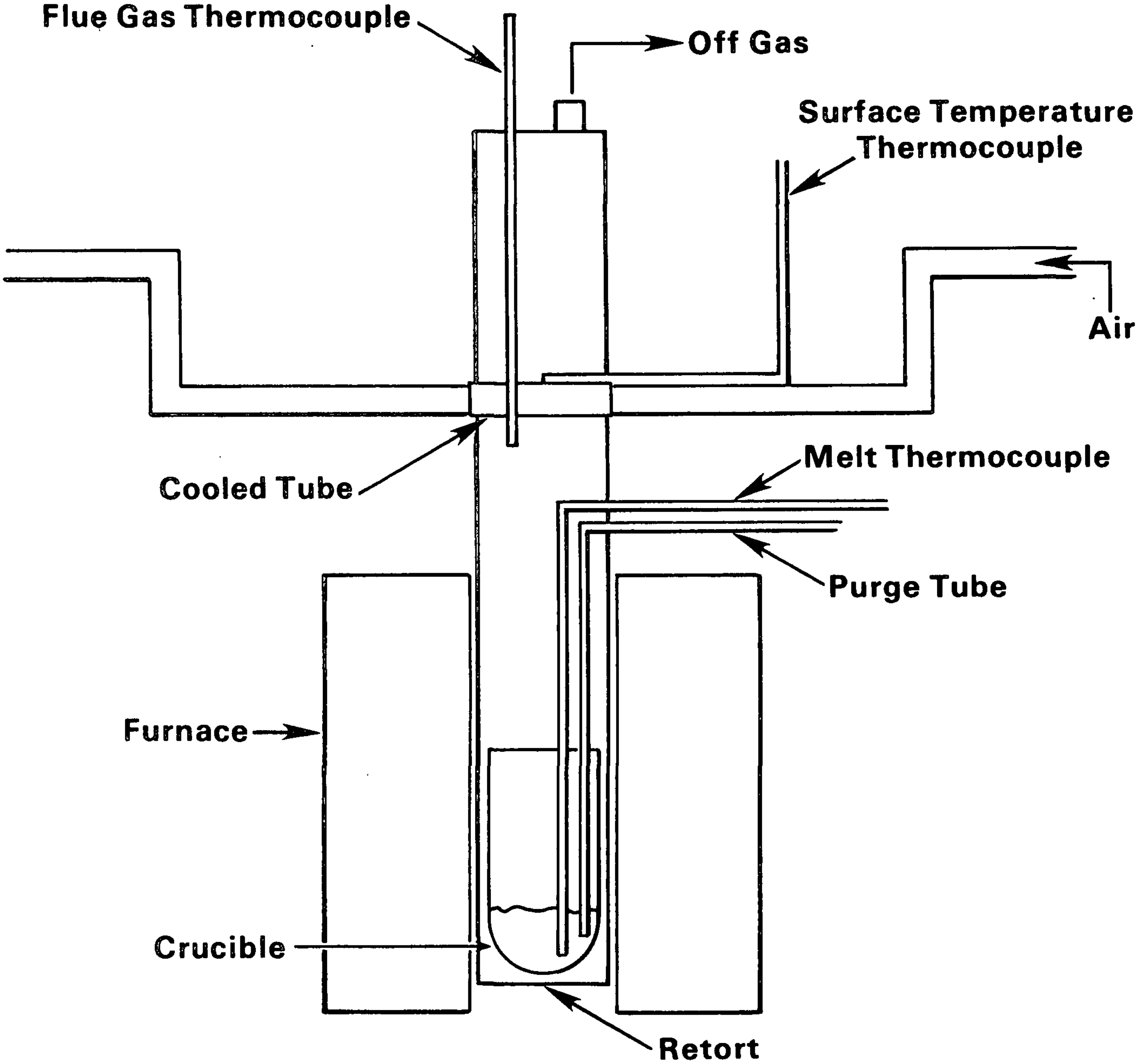
Objectives:

1) Determine Mechanism for Sodium Carbonate Particle Deposition on Cooled Tube

   a) Gas Temperature
   b) Probe Temperature
   c) Gas Flow Rate
   d) Particle Concentration

2) Examine Effects of

   a) Sulfur Species
   b) Potassium
   c) Chloride



Experimental Apparatus for Fume Deposition Study

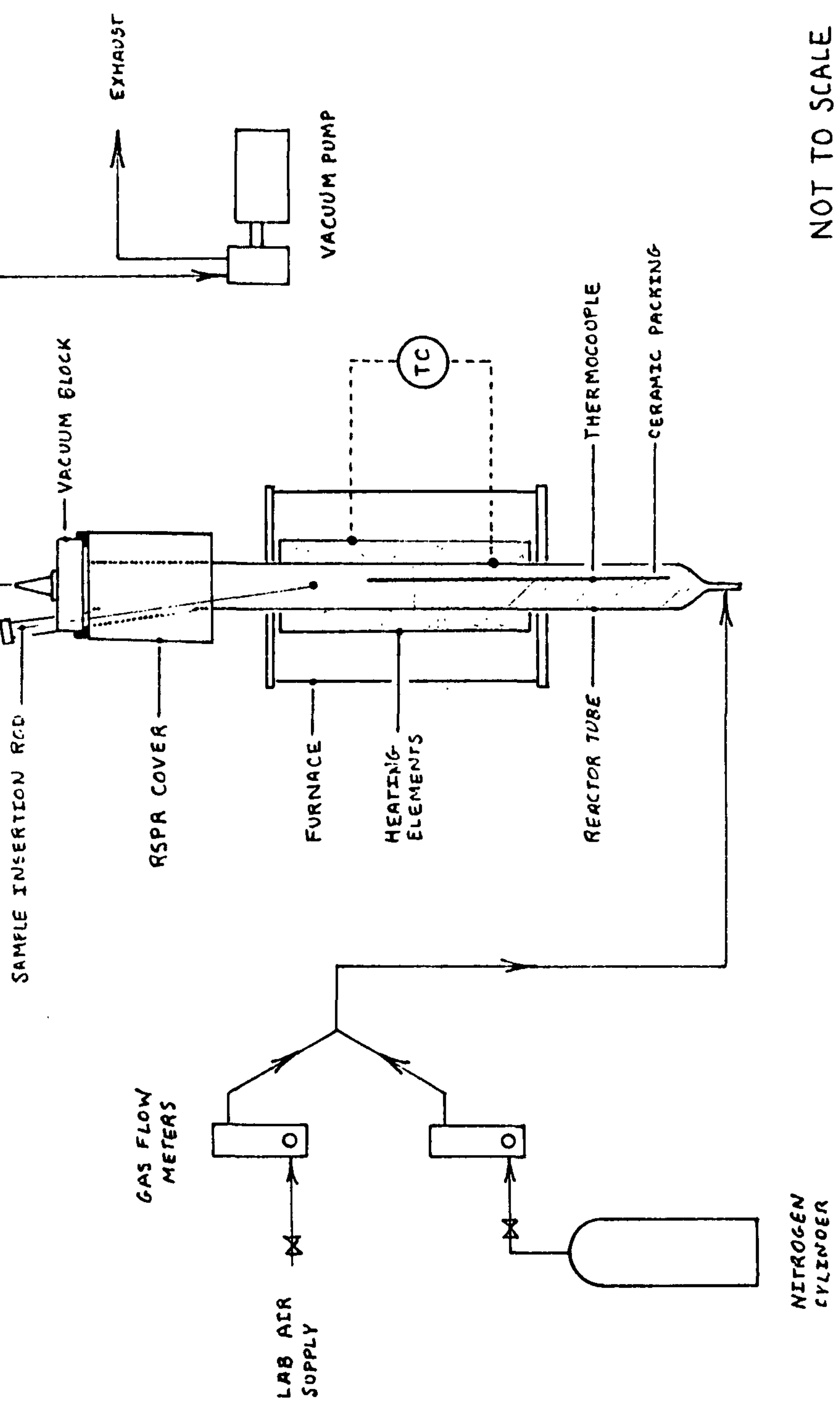
Christopher L. Verrill, Ph.D. - Starting September 1987

FUME GENERATION FROM BLACK LIQUOR BURNING

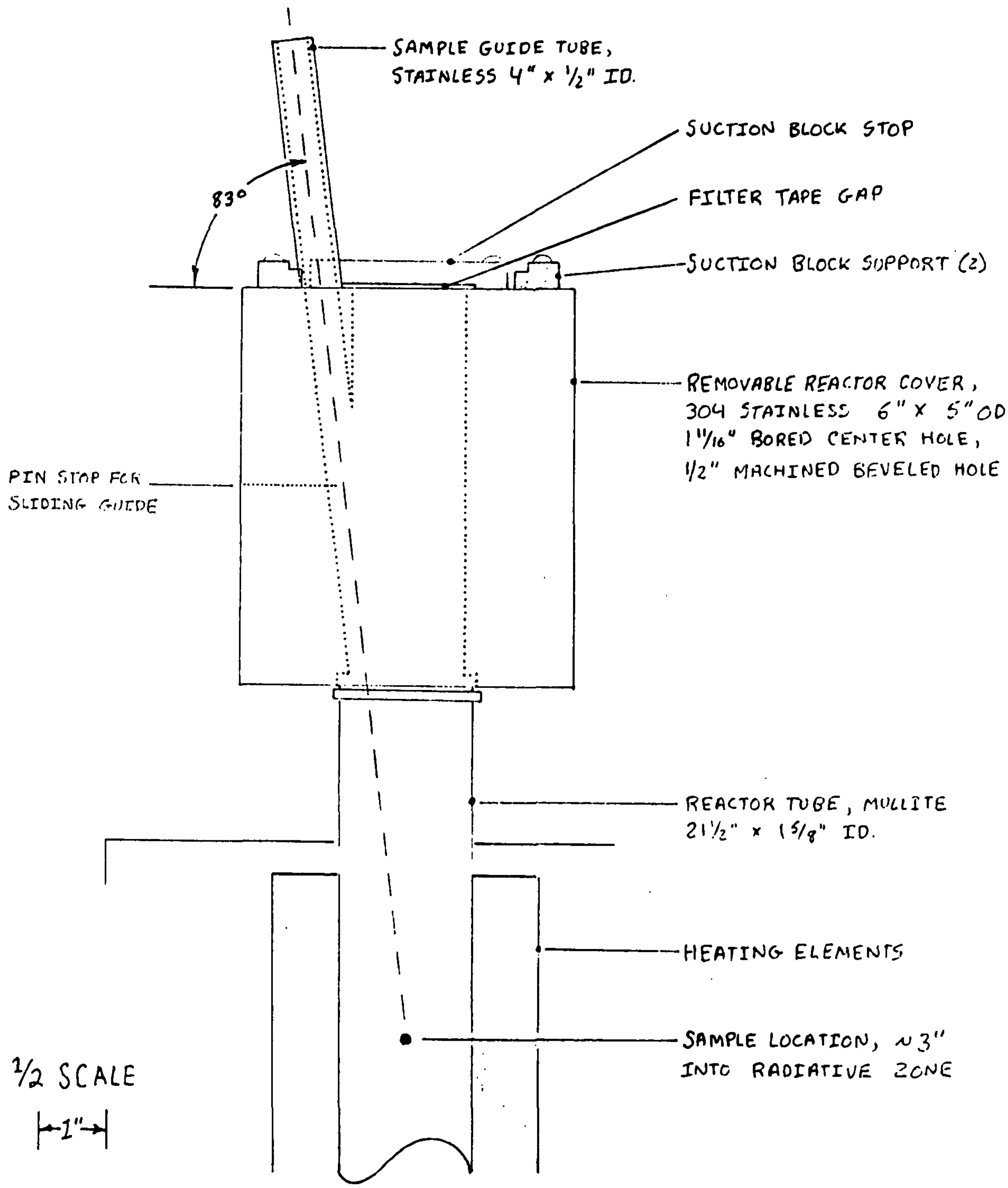
OBJECTIVES

1) Examine fume generation during different stages of burning

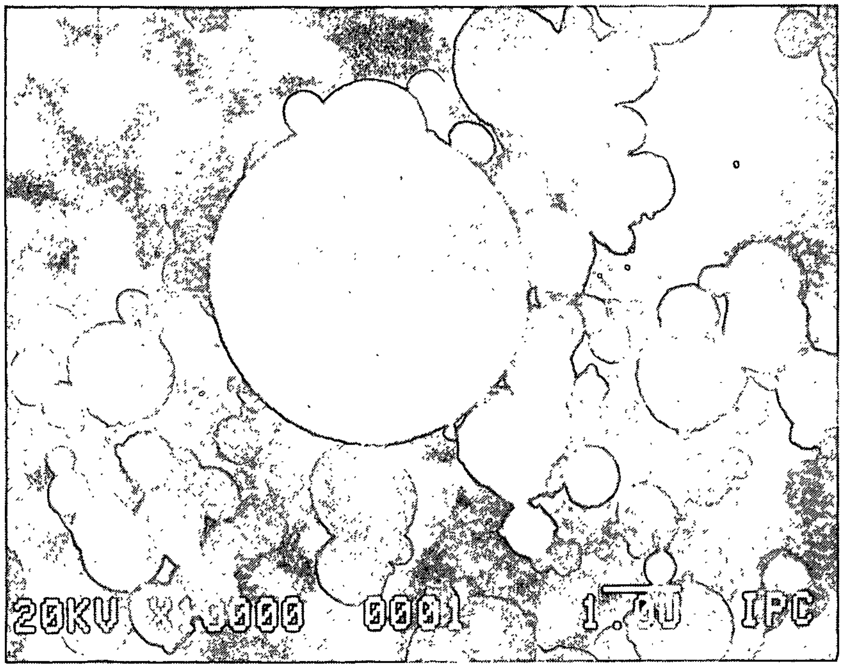
2) Determine the mechanism of fume generation during black liquor droplet burning



Experimental System



Design of RSPR Cover (side view)



High Magnification of Fume from Run #4

Background Area of Filter from Run #4

Other Students

1) Gregg Aiken, Ph.D. - Char Bed Combustion
   a) Model CO/CO_2 Ratio

2) John Fuller, M.S. - Effect of Nonprocess Elements on Lime Nodulization

3) Gregg Maule, M.S. - Study of the Reaction of Sulfur Dioxide with Sodium Carbonate Fume Particles

4) Joseph Kubale, M.S.- Investigation of Laser Techniques for the Determination of Fume Particle Concentrations and Size Distribution

Hydrogen Reactions with Na_2CO_3/Na_2SO_4 Melts

1) $H_2 + Na_2CO_3 \rightleftharpoons 2NaOH + CO$ (liquid phase)

2) $H_2O + Na_2CO_3 \rightleftharpoons 2NaOH + CO_2$ (liquid phase)

3) $CO + 1/4Na_2SO_4 \rightleftharpoons 1/4Na_2S + CO_2$ (liquid phase)

4) $H_2 + 1/4Na_2SO_4 \rightleftharpoons 1/4Na_2S + H_2O$ (liquid phase)

5) $H_2O + CO \rightleftharpoons H_2 + CO_2$ (gas phase)

OBJECTIVE: Determine the Significance of These Reactions in Kraft Furnace

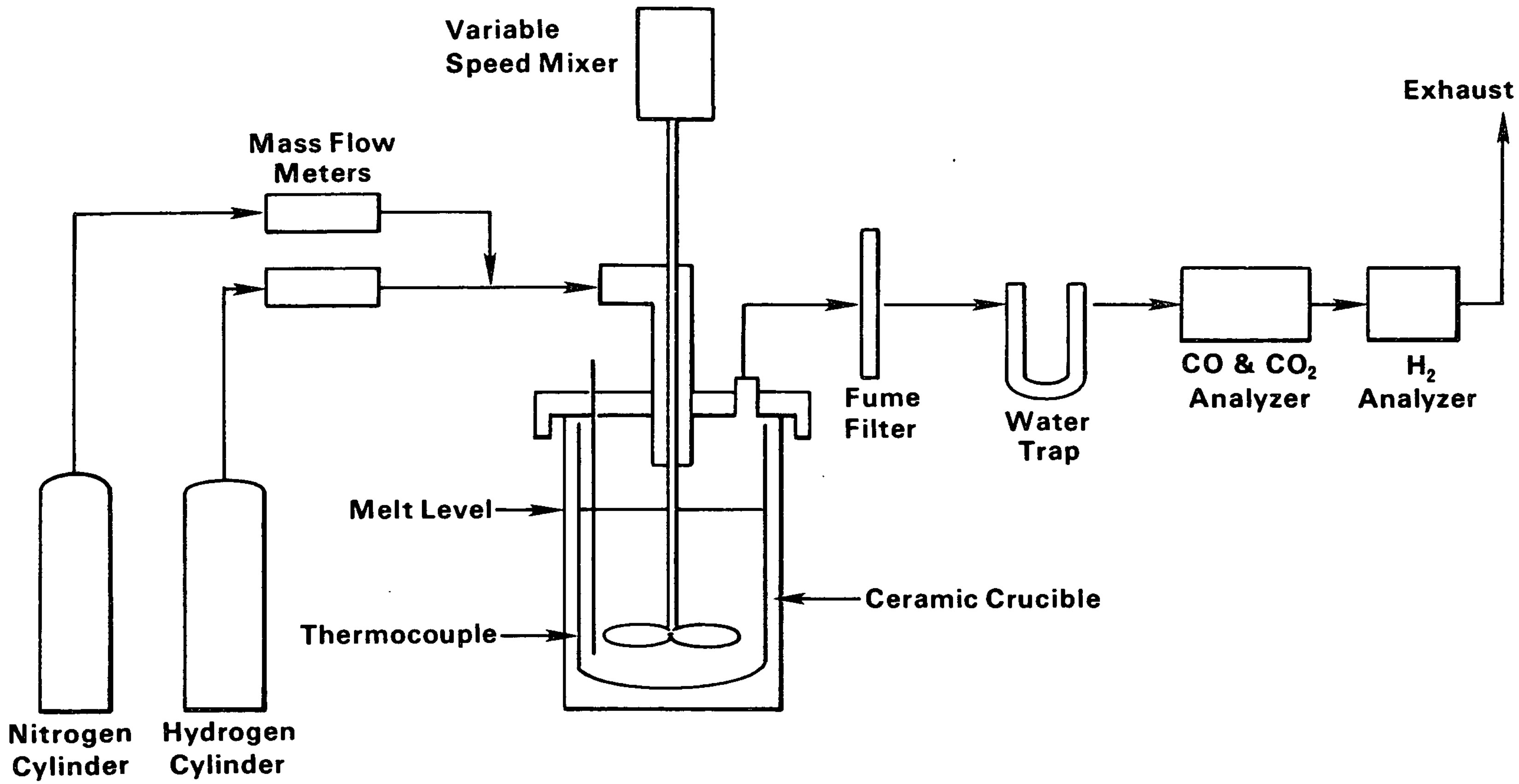
a) Rate Limiting Step

b) Relative Rates

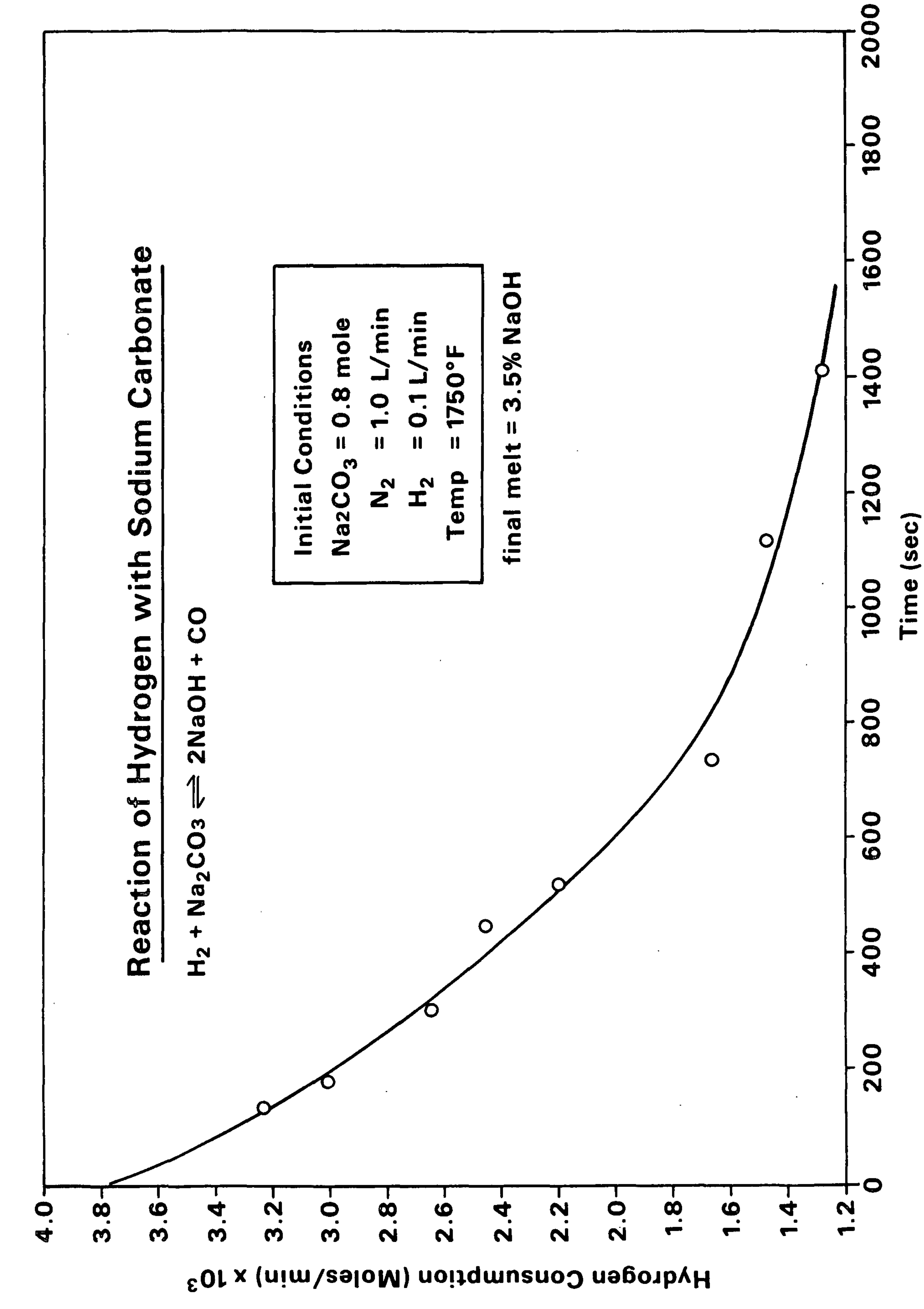
c) NaOH Formation

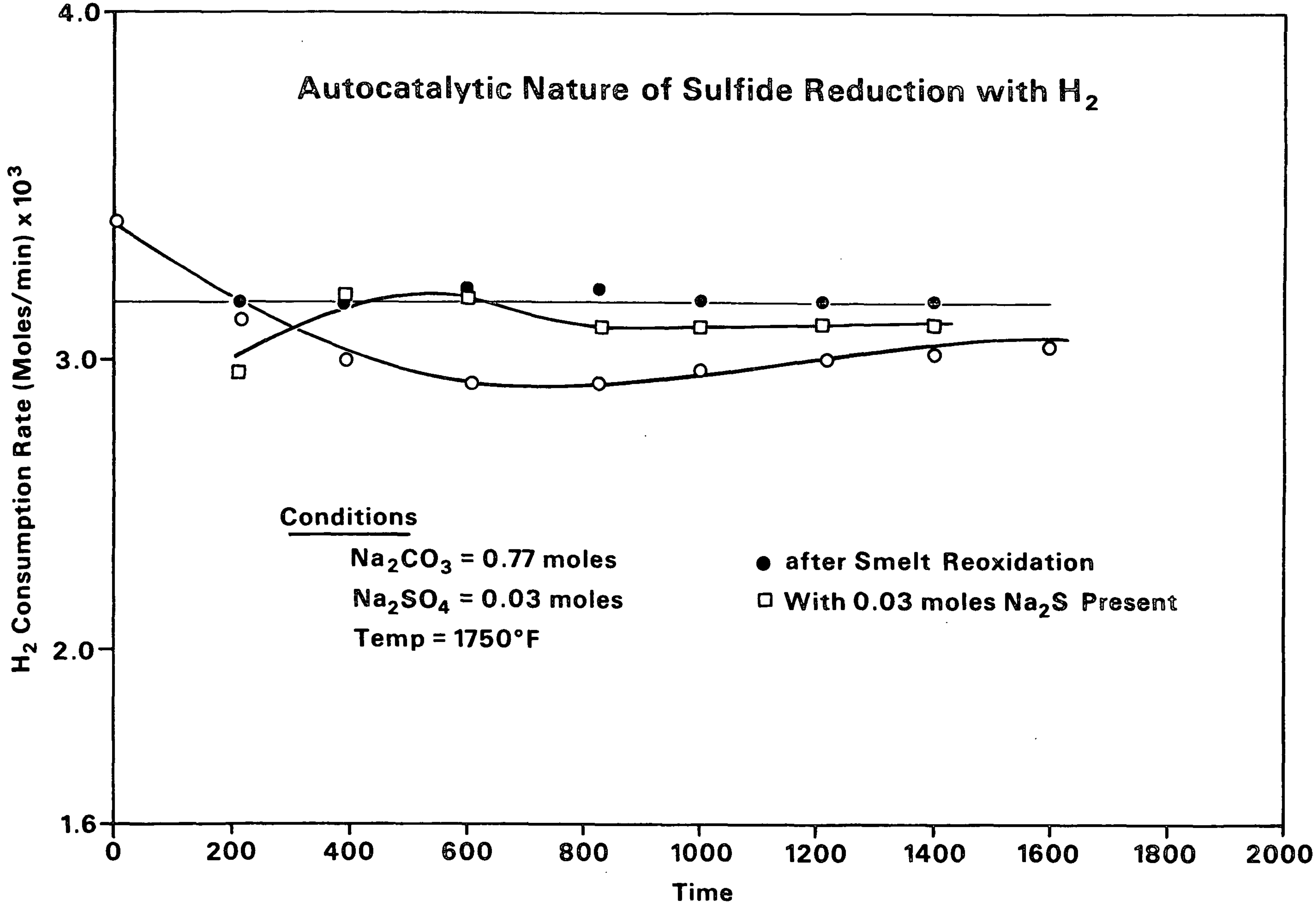
d) Contribution to Sulfate Reduction

c) Effect on Vaporization Processes



Experimental System for Hydrogen Reactions


Reaction of Hydrogen with Sodium Carbonate
$H_2 + Na_2CO_3 \rightleftharpoons 2NaOH + CO$
Initial Conditions
Na_2CO_3 = 0.8 mole
N_2 = 1.0 L/min
H_2 = 0.1 L/min
Temp = 1750°F
final melt = 3.5% NaOH
Hydrogen Consumption (Moles/min) x 10^3
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
Time (sec)
0
200
400
600
800
1000
1200
1400
1600
1800
2000


Autocatalytic Nature of Sulfide Reduction with H_2
H_2 Consumption Rate (Moles/min) x 10^3
4.0
3.0
2.0
1.6
0
200
400
600
800
1000
1200
1400
1600
1800
2000
Time
Conditions
Na_2CO_3 = 0.77 moles
Na_2SO_4 = 0.03 moles
Temp = 1750°F
● after Smelt Reoxidation
□ With 0.03 moles Na_2S Present

BLACK LIQUOR BURNING

FALL REPORT TO PAC

TASK OF PROJECT 3473-1

PRESENTATION OUTLINE

DAVE CLAY	INTRODUCTION AND INTERESTING DEVELOPMENTS
MARK ROBINSON	DRYING
KATHY CRANE	VOLATILES AND CHAR BURNING
DAVE CLAY	COLLABORATION WITH M. HUPA AND PROJECT PLANS

OBJECTIVE

CHARACTERIZE THE BURNING PHENOMENA OF A VARIETY OF BLACK LIQUORS USING QUANTITATIVE TEST METHODS.

STAGES OF BURNING

DRYING

VOLATILES BURNING

CHAR BURNING

SMELT COALESCENCE

RESEARCH APPROACH

FUNDAMENTAL STUDIES

o DRYING	M. ROBINSON
o SWELLING	P. MILLER
o BURNING	B. MORELAND
	K. CRANE
o SULFUR RELEASE	J. CANTRELL

SURVEY STUDIES

- o ANALYTICAL TESTS
- o BURNING TESTS

COLLABORATIVE STUDIES

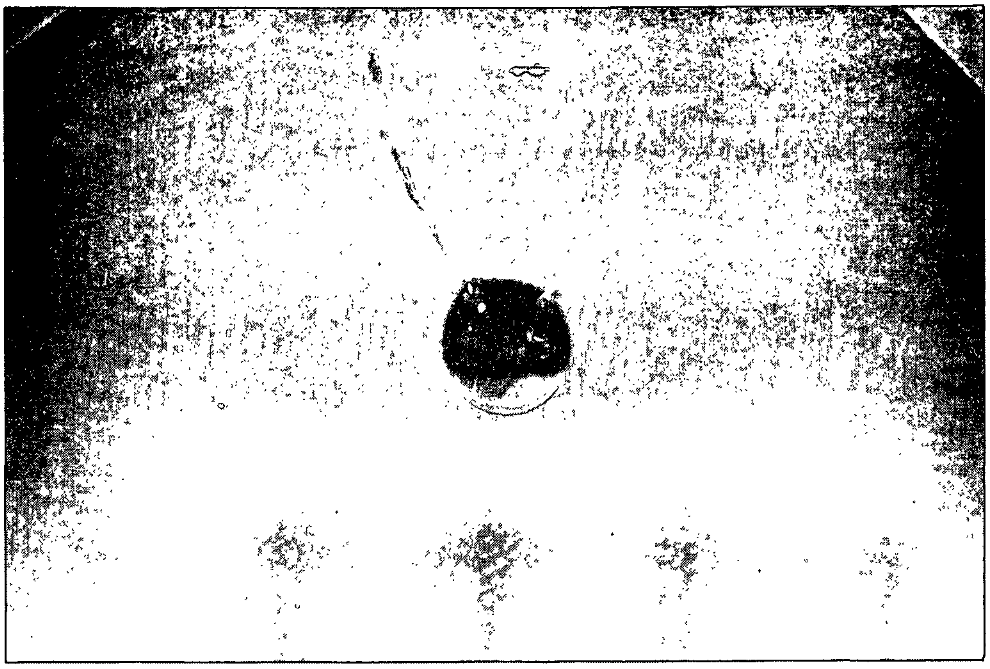
- o MIKKO HUPA
- o WEYERHAEUSER PAPER COMPANY

Selective Analyses to Check on Tall Oil

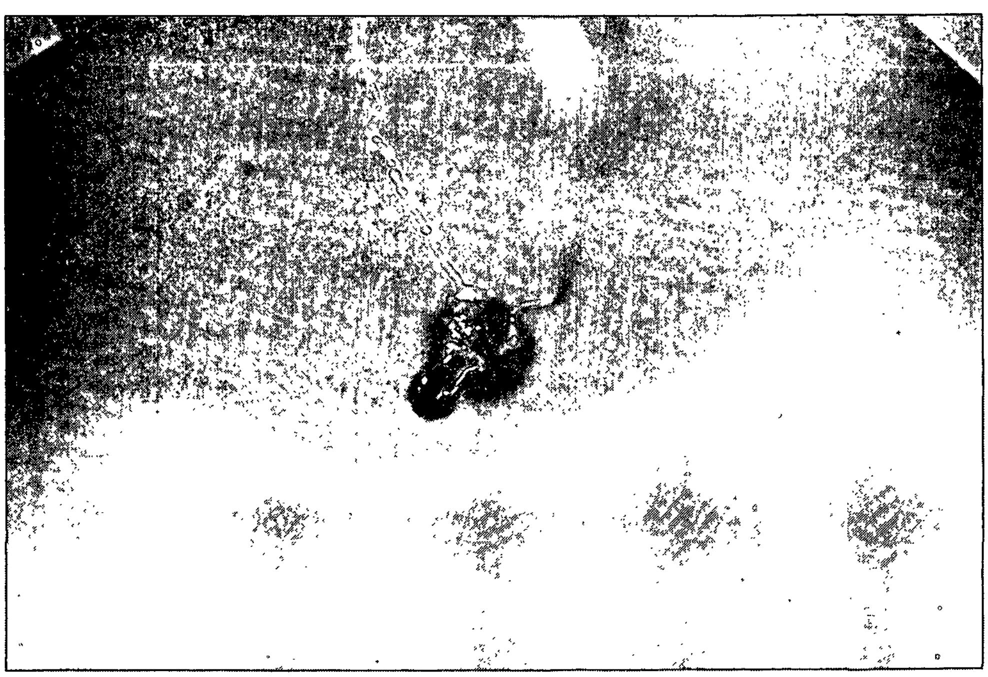
- Four liquors from a high swelling mill
- Two additional mill liquors - one low and one medium
- Tall oil significantly
  - .. increased time from ignition to maximum volume (> 95% significant)
  - .. decreased pyrolysis swollen volume (> 90% significant)
- Tall oil content measurements are required even on previously skimmed liquors.

CHARACTERIZATION OF BLACK LIQUOR DROPLET DRYING IN AIR AND SUPERHEATED STEAM

MARK L. ROBINSON
PH.D. CANDIDATE



BLACK LIQUOR DROPLET SUSPENDED FROM FINE THERMOCOUPLE



DROPLET BURSTING IN AIR DRYING

EXPERIMENTAL APPROACH

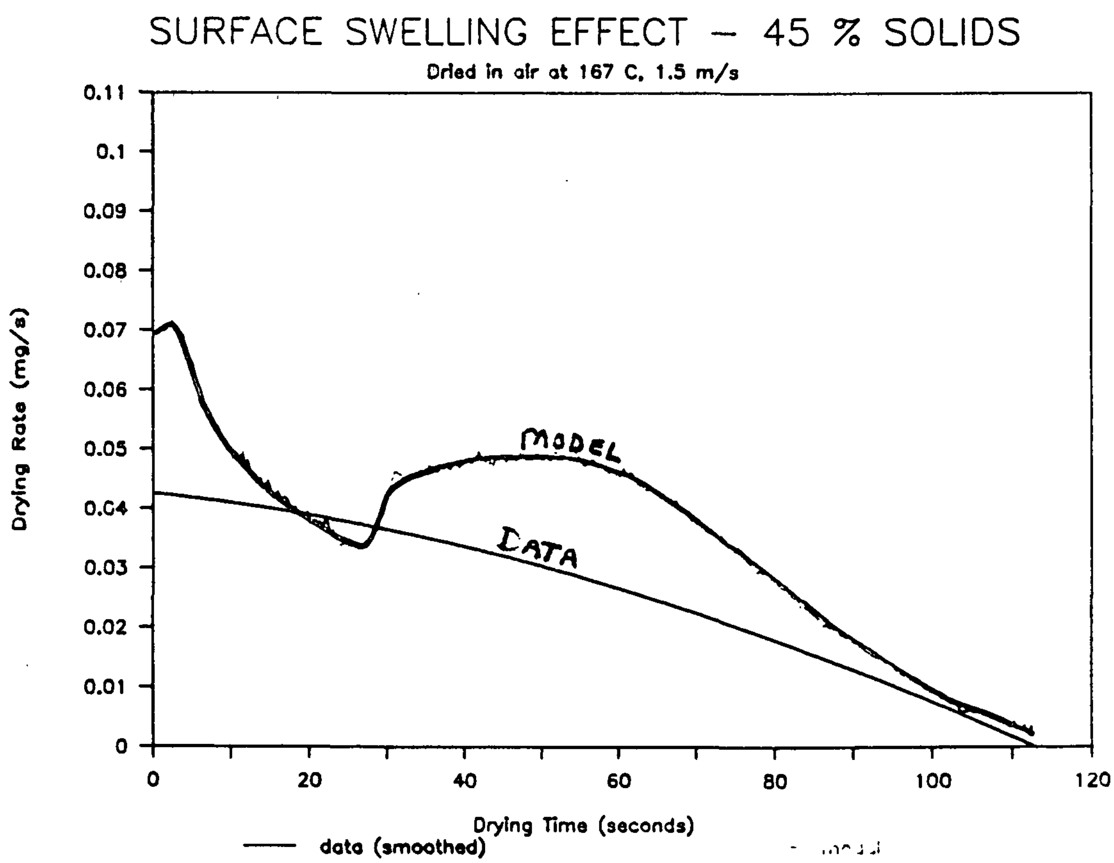
LOW TEMPERATURE DRYING

-- AVOID PYROLYSIS

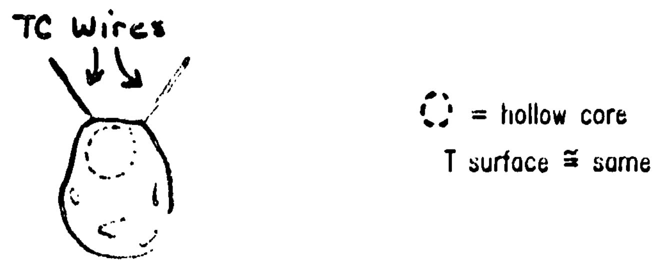
-- OBSERVE AND EXPLAIN PHENOMENA

-- OBTAIN RATE DATA

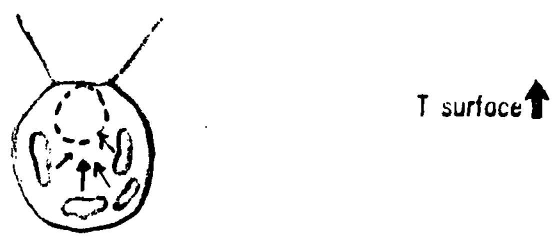
-- APPLY AND EXPAND RESULTS



Heterogeneous Nucleation of Water Vapor in an Air Dried Black Liquor Droplet

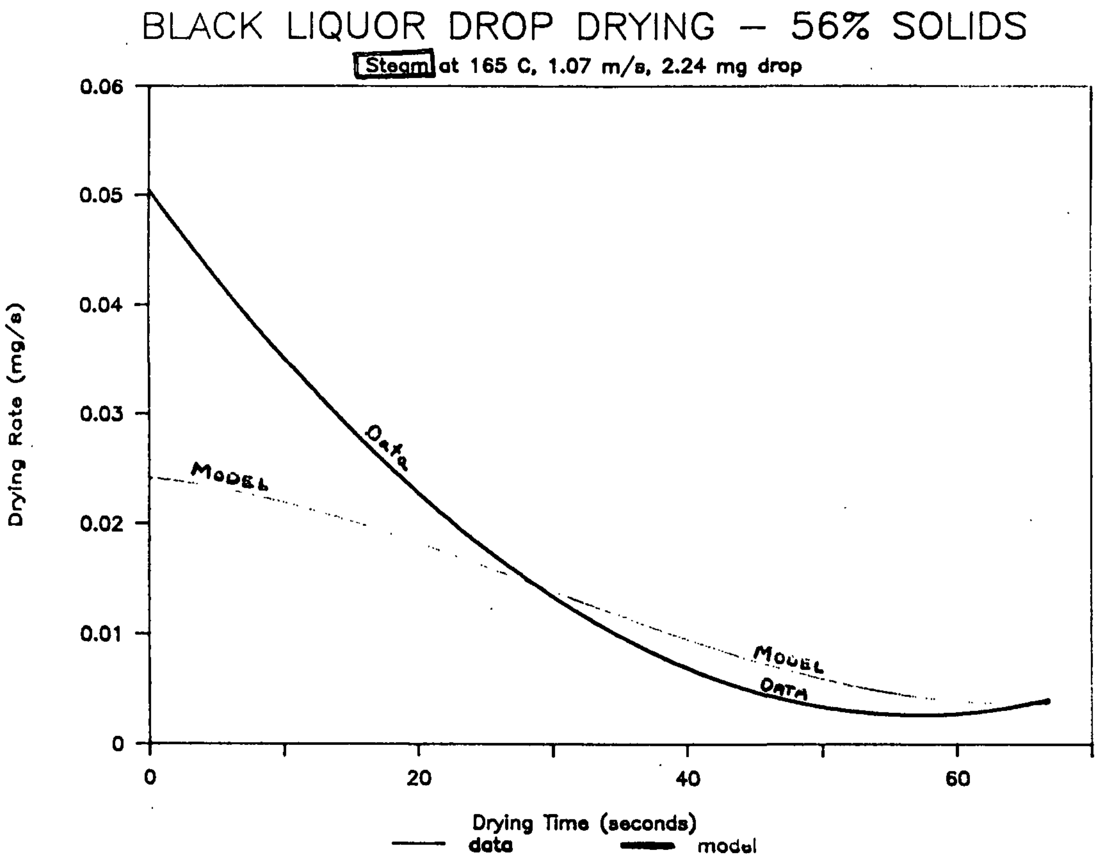


Step 1 Vapor forms at multiple nucleation sites



Step 2 Vapor pocket grows and droplet inflates

Step 3 Hollow core and vapor pocket coalesce; inflated drop bursts and shrinks



CONCLUSIONS

1. ACCURATE CONTINUOUS DATA WERE OBTAINED.
2. IN AIR, DRYING RATE IS <u>NOT</u> ENHANCED BY SWELLING.
3. IN STEAM, DRYING RATE IS GREATLY ENHANCED BY SWELLING.
4. HETEROGENEOUS VAPOR NUCLEATION OCCURS IN BLACK LIQUOR DRIED IN AIR ABOVE THE BOILING POINT.
5. EXTERNAL HEAT TRANSFER SHOULD DETERMINE DRYING RATE IN HIGH TEMPERATURE ENVIRONMENTS.

AN OVERALL MODEL FOR THE COMBUSTION OF A SINGLE DROPLET OF KRAFT BLACK LIQUOR

KATHERINE A. CRANE

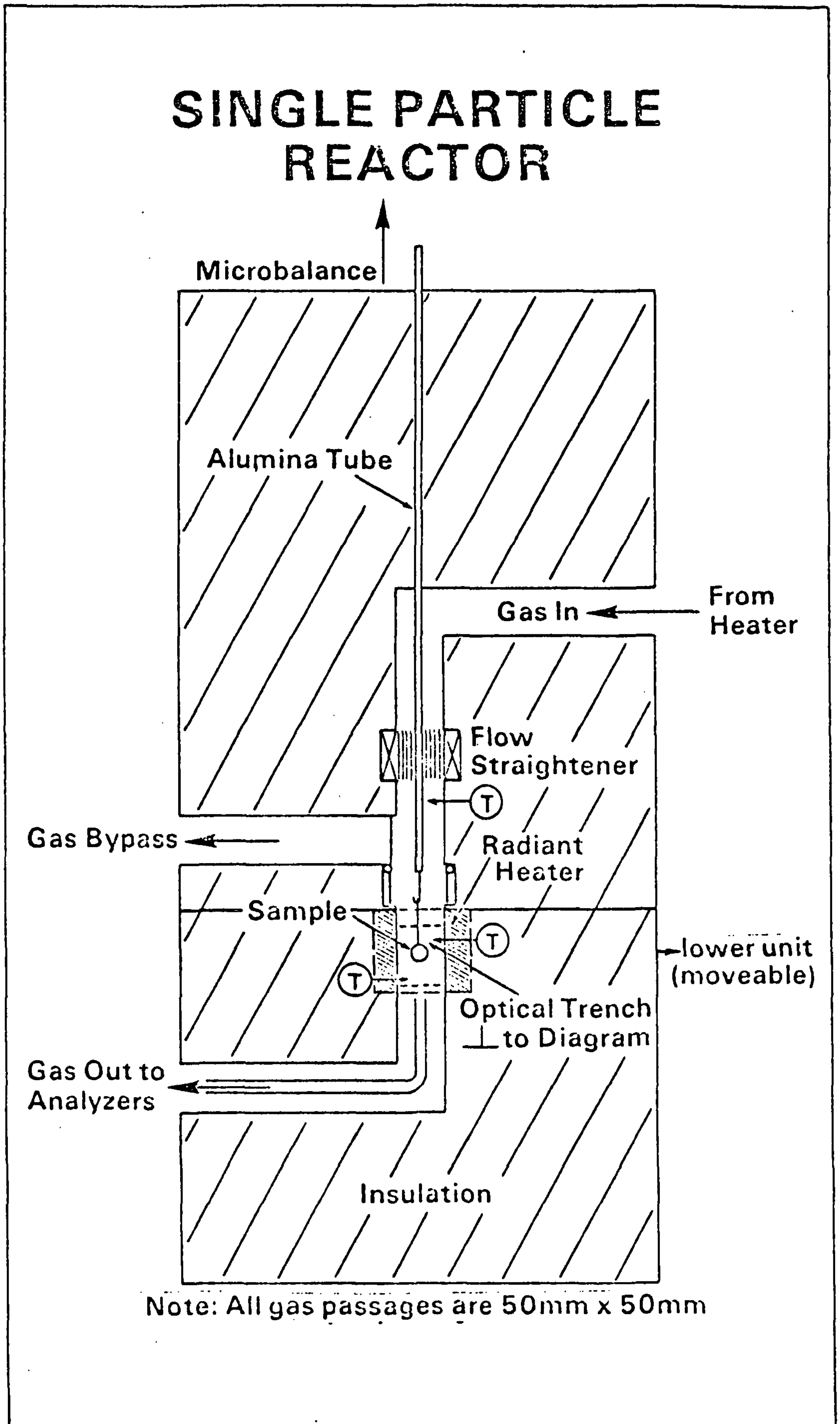
<u>EXPERIMENTAL</u>

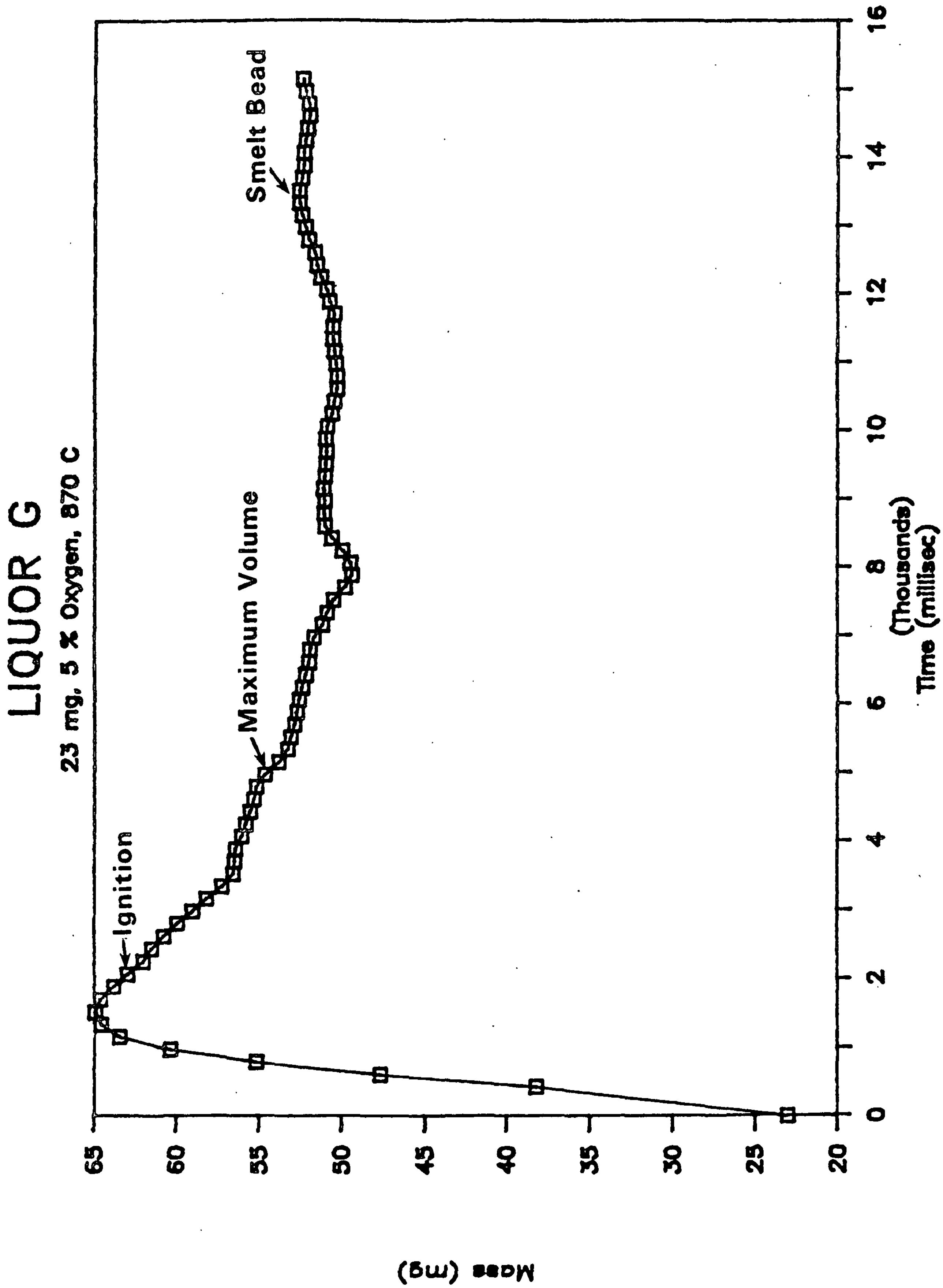
3 x 3 ! WITH 3 REPLICATIONS

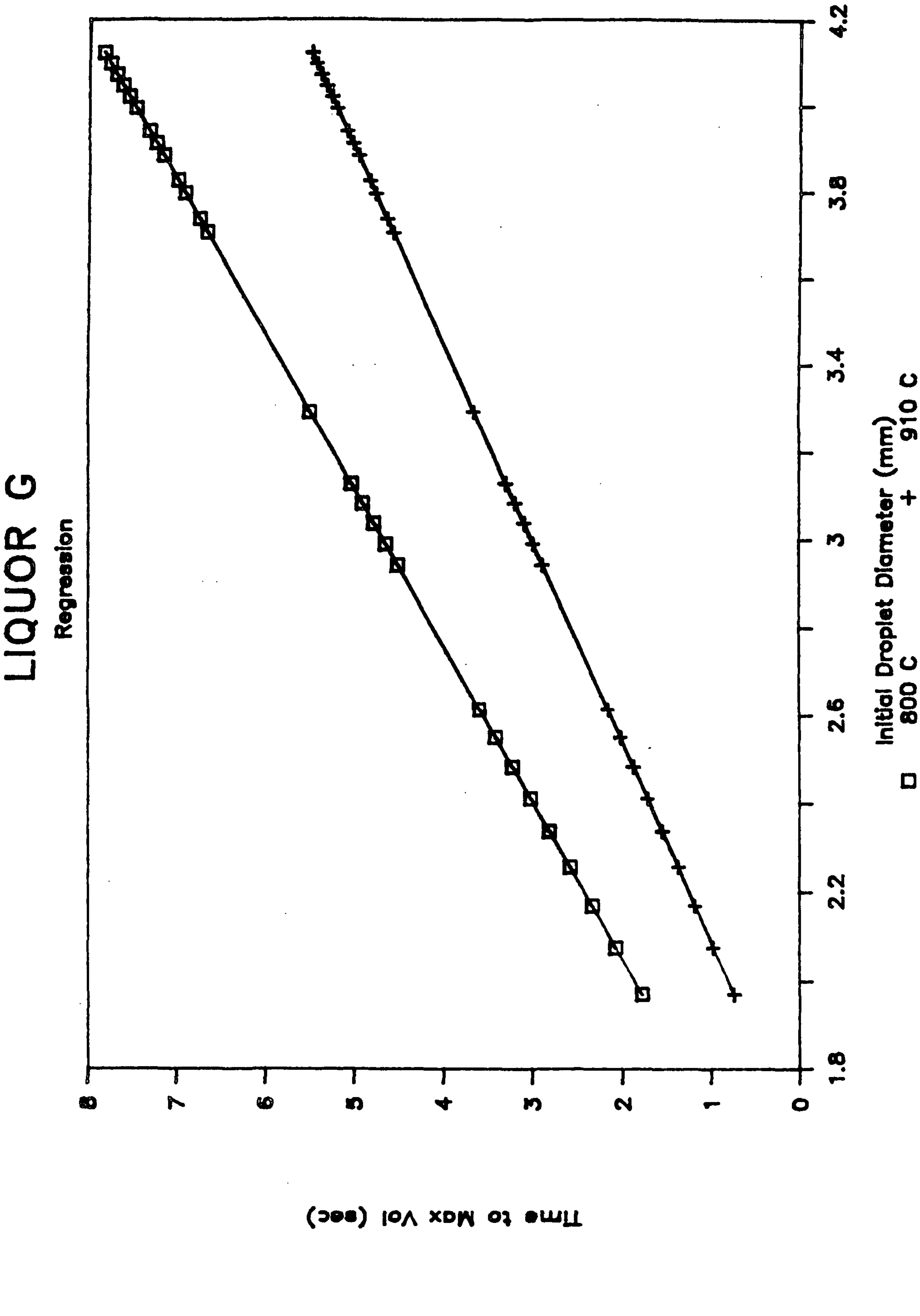
GAS TEMPERATURE: 800, 870, 910°C

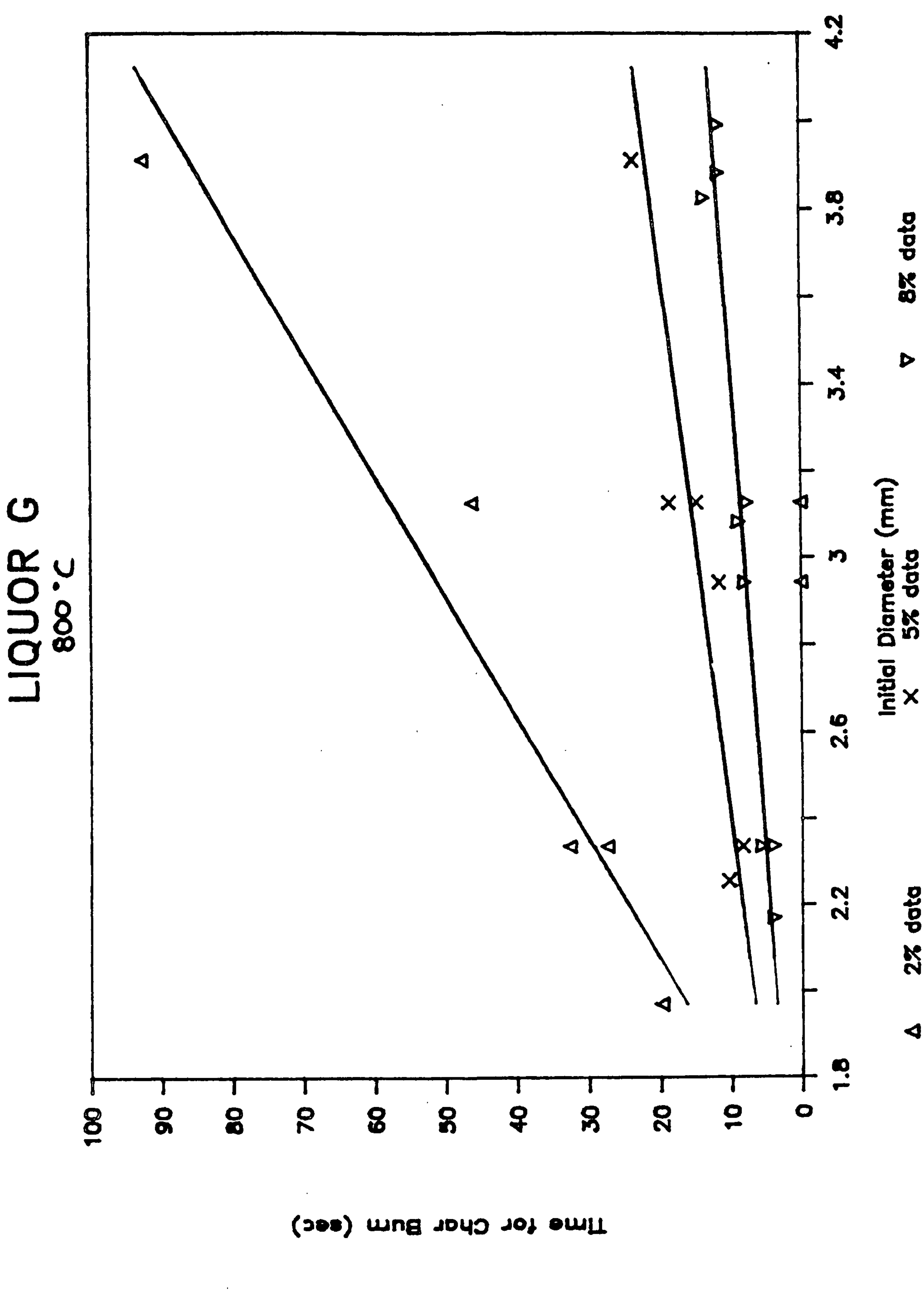
OXYGEN CONCENTRATION: 2, 5, 8%

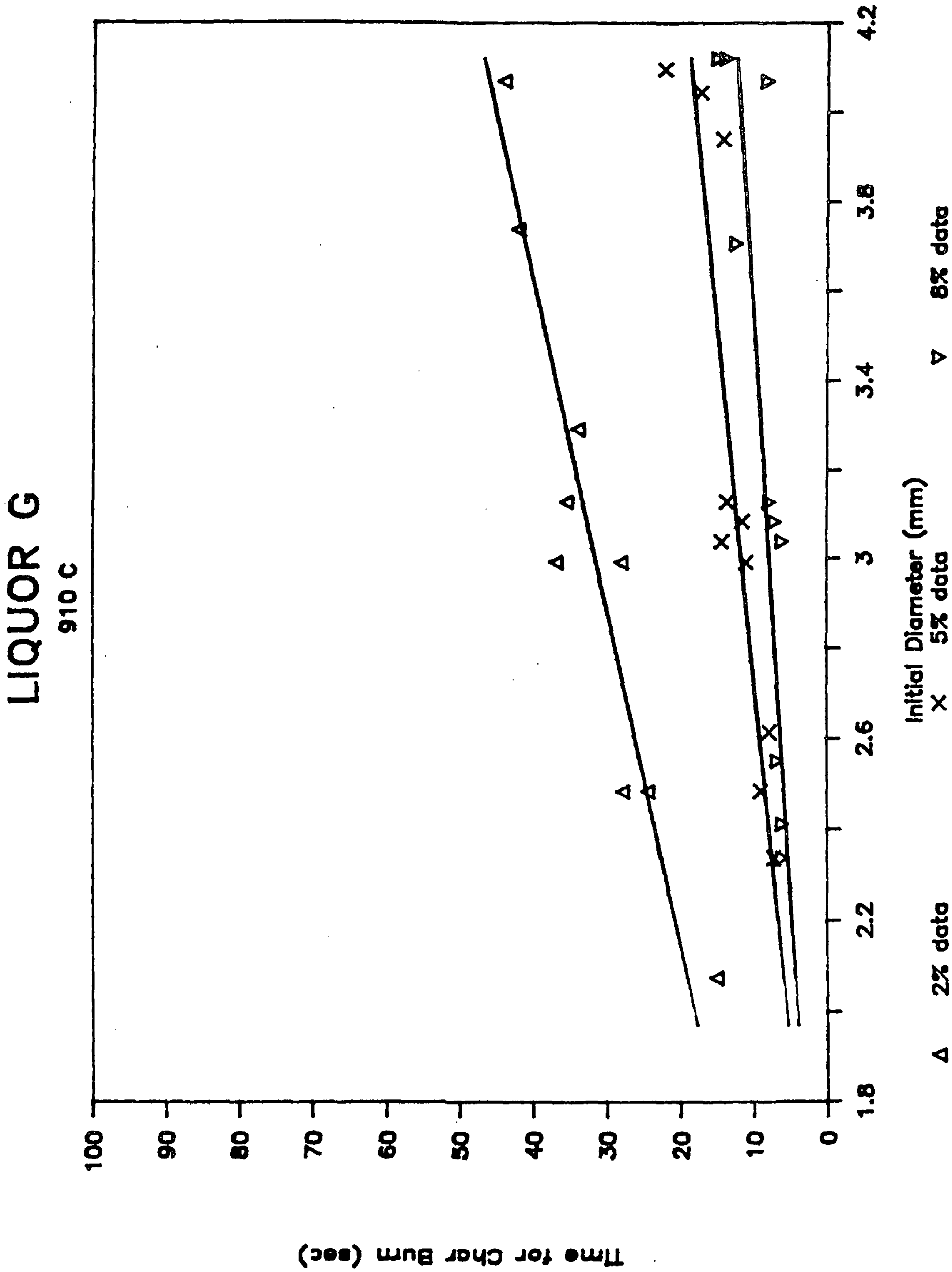
INITIAL DROPLET SIZE: 1.5, 3.0, 4.0MM

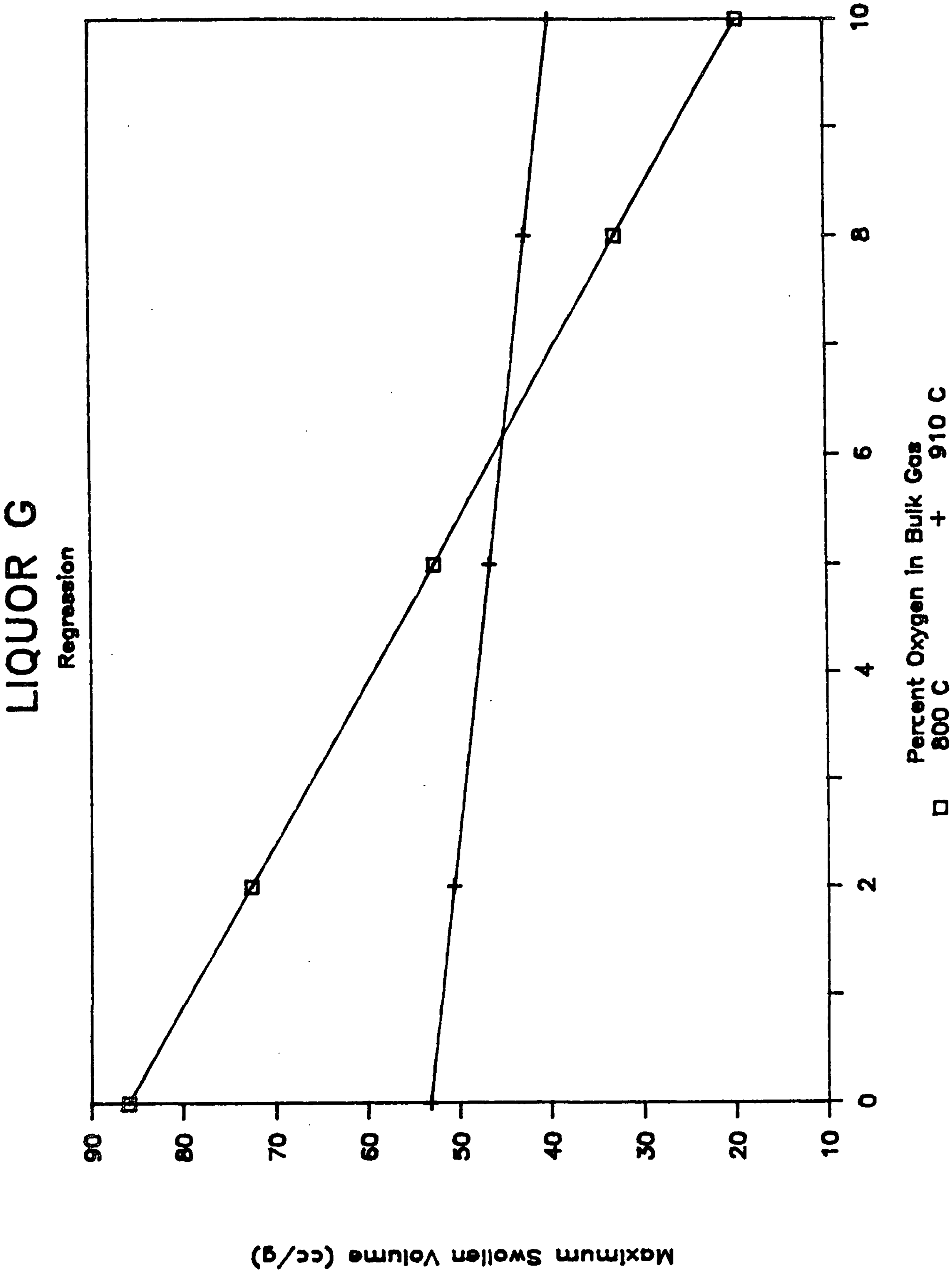

SINGLE PARTICLE REACTOR
Microbalance
Alumina Tube
Gas In
From Heater
Flow Straightener
T
Gas Bypass
Radiant Heater
Sample
T
T
lower unit (moveable)
Optical Trench ⊥ to Diagram
Gas Out to Analyzers
Insulation
Note: All gas passages are 50mm x 50mm


LIQUOR G
23 mg, 5 % Oxygen, 870 C
Ignition
Maximum Volume
Smelt Bead
Mass (mg)
65
60
55
50
45
40
35
30
25
20
0
2
4
6
8
10
12
14
16
Time (Thousands) (millisec)


LIQUOR G
Regression
Time to Max Vol (sec)
0
1
2
3
4
5
6
7
8
Initial Droplet Diameter (mm)
1.8
2.2
2.6
3
3.4
3.8
4.2
□ 800 C
+ 910 C


LIQUOR G
800 °C
Time for Char Burn (sec)
Initial Diameter (mm)
△ 2% data
× 5% data
▽ 8% data
100
90
80
70
60
50
40
30
20
10
0
1.8
2.2
2.6
3
3.4
3.8
4.2


LIQUOR G
910 C
Time for Char Burn (sec)
100
90
80
70
60
50
40
30
20
10
0
1.8
2.2
2.6
3
3.4
3.8
4.2
Initial Diameter (mm)
2% data
5% data
8% data



LIQUOR G
Regression
Maximum Swollen Volume (cc/g)
90
80
70
60
50
40
30
20
10
0
2
4
6
8
10
Percent Oxygen In Bulk Gas
□ 800 C
+ 910 C

CONCLUSIONS

- VOLATILES EVOLUTION RATE IS DEPENDENT ON TEMPERATURE AND PARTICLE SIZE.
- TIME TO MAXIMUM VOLUME IS DEPENDENT ON TEMPERATURE AND PARTICLE SIZE.
- TIME FOR CHAR BURN IS DEPENDENT ON OXYGEN CONCENTRATION AND INITIAL PARTICLE SIZE, ESPECIALLY BELOW 5% OXYGEN.
- TIME FOR CHAR BURN IS DEPENDENT ON TEMPERATURE AT 2% OXYGEN.
- MAXIMUM SWOLLEN VOLUME IS STRONGLY DEPENDENT ON OXYGEN AT 800°C AND WEAKLY DEPENDENT ON OXYGEN AT 910°C.

COLLABORATIVE WORK WITH DR.MIKKO HUPA

MEETING AT IPC JANUARY 21, 1987
EXCHANGE OF 8 LIQUORS EACH
REVIEWED HUPA'S FILMS
DEVELOP WORK PLAN

VIDEO TAPE OF SINGLE PARTICLE FUMING IN
A RADIANTLY HEATED AIR ENVIRONMENT

PROJECT WORK PLAN

DRYING STUDIES (ROBINSON & DOE)	COMPLETE	SUMMER 1987
BURNING STUDIES (CRANE & DOE)	ON-GOING	
SULFUR RELEASE STUDIES (HARPER & DOEO	ON-GOING	
COMPARISON OF BURNING TEST ETHODS (IPC & HUPA)	COMPLETE	FALL 1987
CONTROLLED LIQUOR BURNING (IPC & HUPA)	COMPLETE	FALL 1987
BURNING PHENOMENA FUNDAMENTALS (IPC & HUPA)	COMPLETE	FALL 1988

Project 3473-6

Dave Clay

Steve Lien

FUNDAMENTAL STUDIES OF BLACK LIQUOR COMBUSTION

(FALL REPORT TO PAC)
PROJECT 3473-6

PRESENTATION OUTLINE

DAVE CLAY	OVERVIEW STATUS RESULTS DIRECTION
STEVE LIEN	TEST EQUIPMENT

OBJECTIVES

DEVELOP BLACK LIQUOR COMBUSTION REACTORS

APPLY ADVANCED SPECTROSCOPIC TECHNIQUES

OBTAIN FUNDAMENTAL DATA

ACCOMPLISHMENTS
(SINCE OCTOBER 1986)

IPC

UPFLOW IN-FLIGHT TESTING COMPLETE.

REDUCED SULFUR GAS RELEASE FROM SINGLE PARTICLES MEASURED.

INITIAL DRYING MODEL DEVELOPED FOR IN-FLIGHT REACTOR.

EQUIPMENT RECEIVED FOR DOWNFLOW AND BED BURNING STUDIES.

PRELIMINARY DRAFT OF PROGRESS REPORT 2 SUBMITTED TO DOE.

SPONSORSHIP OF AN INDUSTIRAL FELLOW BY THE WEYERHAEUSER COMPANY.

ACCOMPLISHMENTS
(SINCE OCTOBER 1986)

NBS

DYNAMIC NONINTRUSIVE TEMPERATURE MEASUREMENTS OF SINGLE BURNING BLACK LIQUOR DROPLETS.

TEMPERATURE PROFILE MEASUREMENTS IN THE FULL-HEIGHT DPFR COMPLETED.

DYNAMIC PARTICLE SIZE/VELOCITY MEASUREMENTS IN THE FULL-HEIGHT DPFR CONFIGURATION HAS BEGUN.

STATUS

IPC PREPARING FOR DOWNFLOW TESTS.

NBS CONDUCTING LONGER TIME EARLY IN-FLIGHT TESTS.

IN-FLIGHT TEST
GROUP 3

BASE CONDITIONS

LIQUOR FEED: 3 LB/HR (23 GRAM/MIN)
OXIDIZED LIQUOR NO. 41

GAS: AIR
FLOW 4 SCFM (115 STD. LPM)
TEMPERATURE 1675°F (913°C)

INDEPENDENT VARIABLES

SOLIDS: 60.4 TO 66.8%
INJECTOR ID: 1.07 TO 1.73 MM

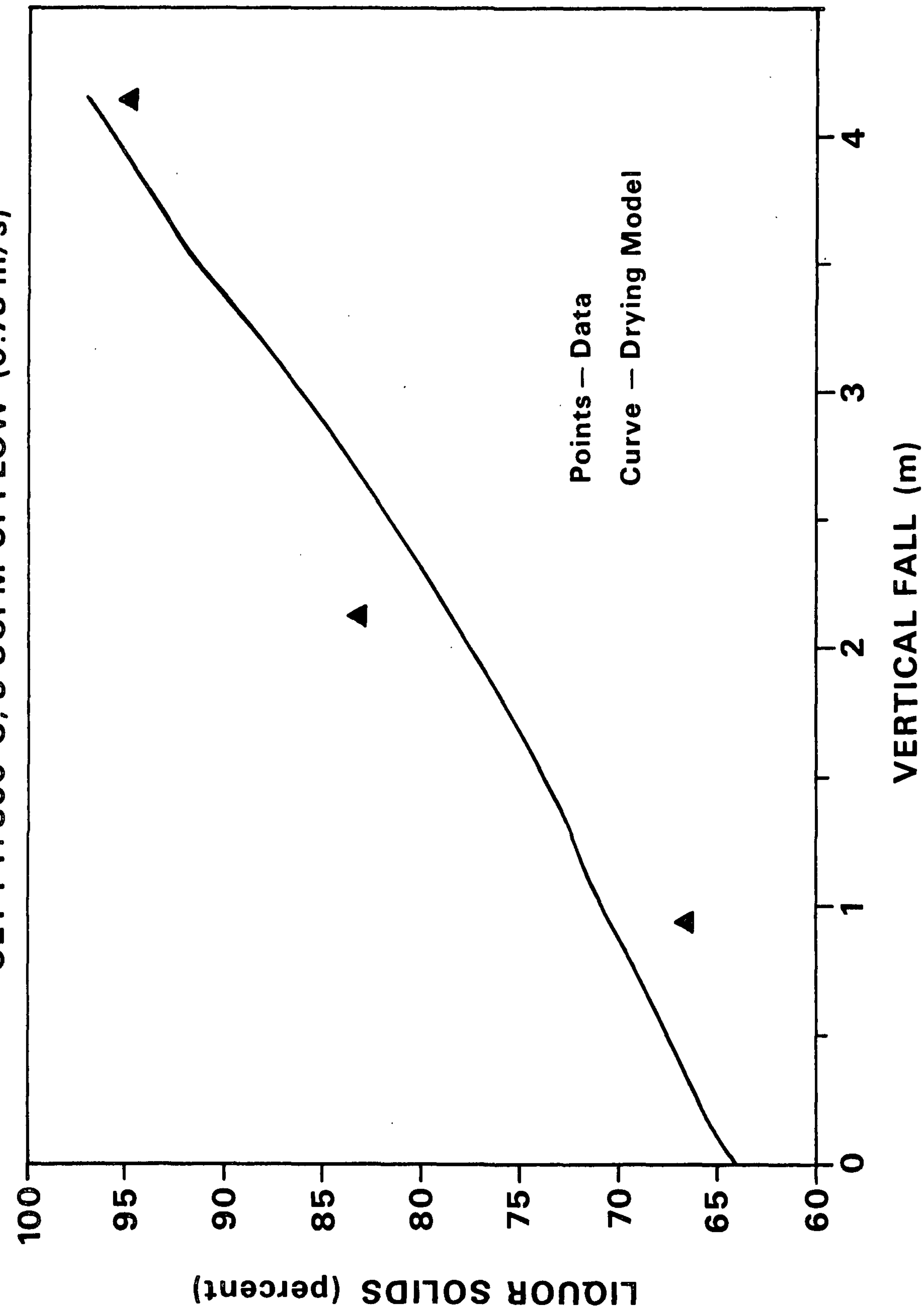
LIQUOR TEMPERATURE: 264-282°F (129-139°C)
DROPLET DIAMETER: 5.2-6.8 MM

RESULTS GROUP 3

- PARTICLE FORMATION POOR. TEST GROUP HAS BEEN REPEATED WITH SECOND LIQUOR BATCH.
- SIGNIFICANT (> 95%) COMPOSITIONAL DEPENDENCIES WERE FOUND WITH FEED SOLIDS AND INJECTION TEMPERATURE.
  - .. HIGHER TEMPERATURES AND LOWER SOLIDS PRODUCED MORE REACTIVE PARTICLES I.E., HIGHER VOLATILES LOSS
    MORE FIXED CARBON
- IMPLIES THAT LIQUOR VISCOSITY (LOWERED BY BOTH OF THE ABOVE EFFECTS) MAY BE A CRITICAL CONTROLLING PARAMETER IN THE RATE OF EARLY IN-FLIGHT PROCESSES.

DOE IN—FLIGHT REACTOR — — B.L. DRYING

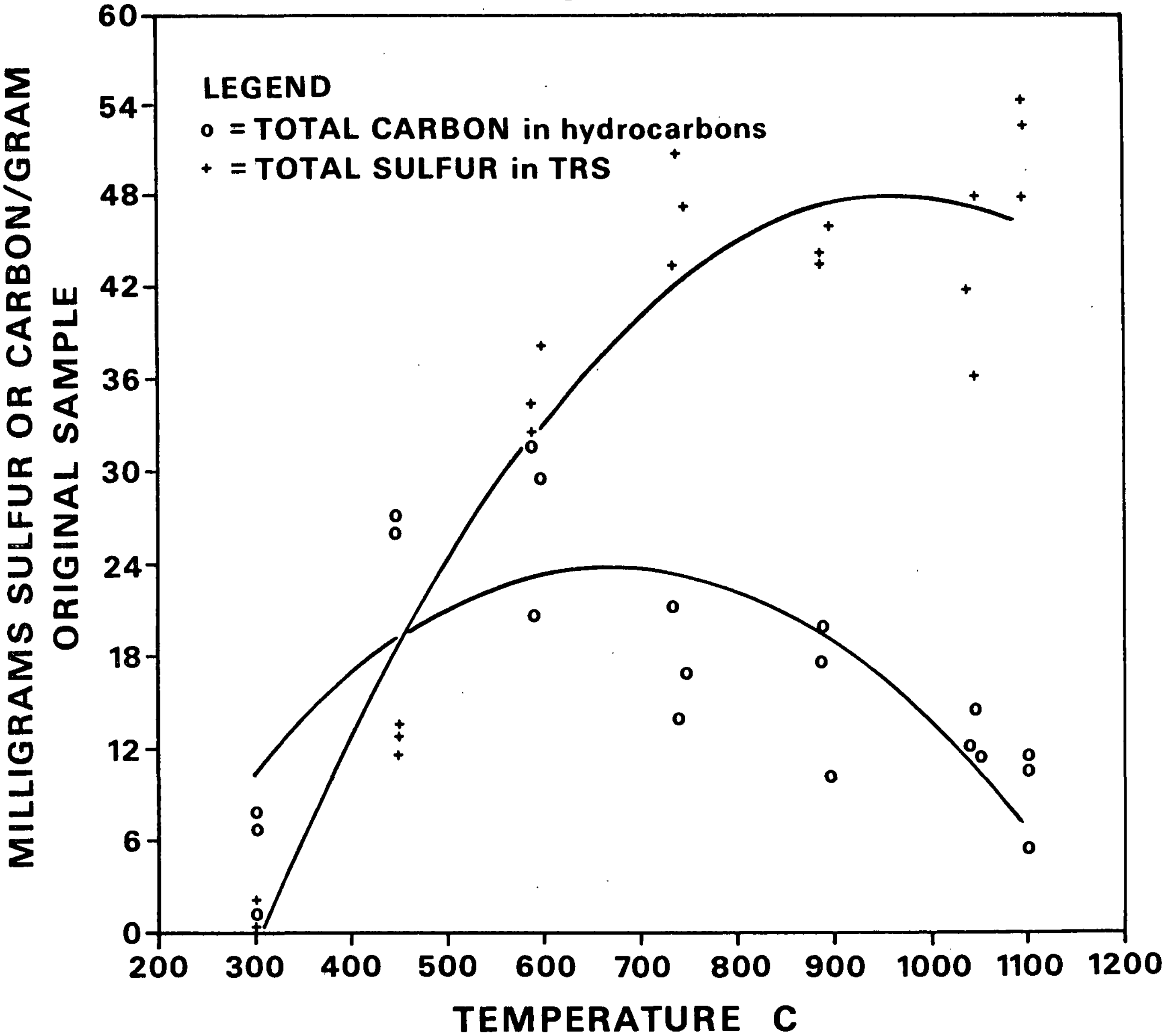
SET PT. 860 C, 3 SCFM UPFLOW (0.73 m/s)



TOTAL HYDROCARBON CARBON AND REDUCED SULFUR RELEASE

Radiant SPR. N_2 atmosphere

B.L. No. 41, 15mg (2.7mm), 67.4% solids



BURNING SINGLE-PARTICLE TEMPERATURE MEASUREMENTS

NBS TWO-COLOR PYROMETER

IPC CONVECTIVE SPR AIR @ 1292°F
KRAFT BLACK LIQUOR @ 66% SOLIDS (2.3 MM)

	TEMPERATURES °F*
FLAMING COMBUSTION	2050 - 2210
END OF FLAME	1830 - 1920
CHAR BURNING	1920 - 2370

*BASED ON INITIAL BACKGROUND INTENSITIES

NEAR TERM DIRECTION

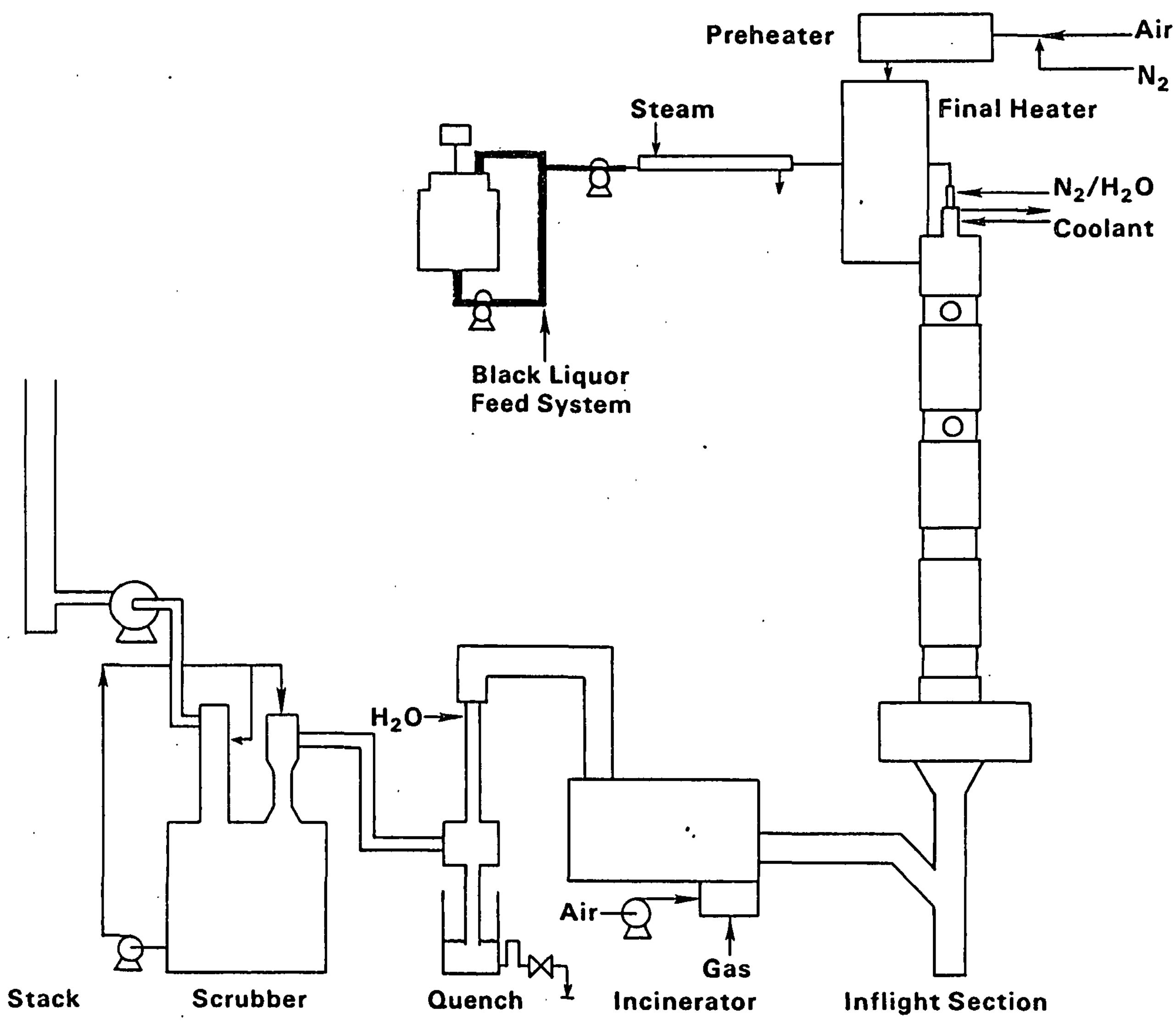
COMPLETE DOE PROGRESS REPORT 2.

CONDUCT DOWNFLOW PROCESS TESTS.

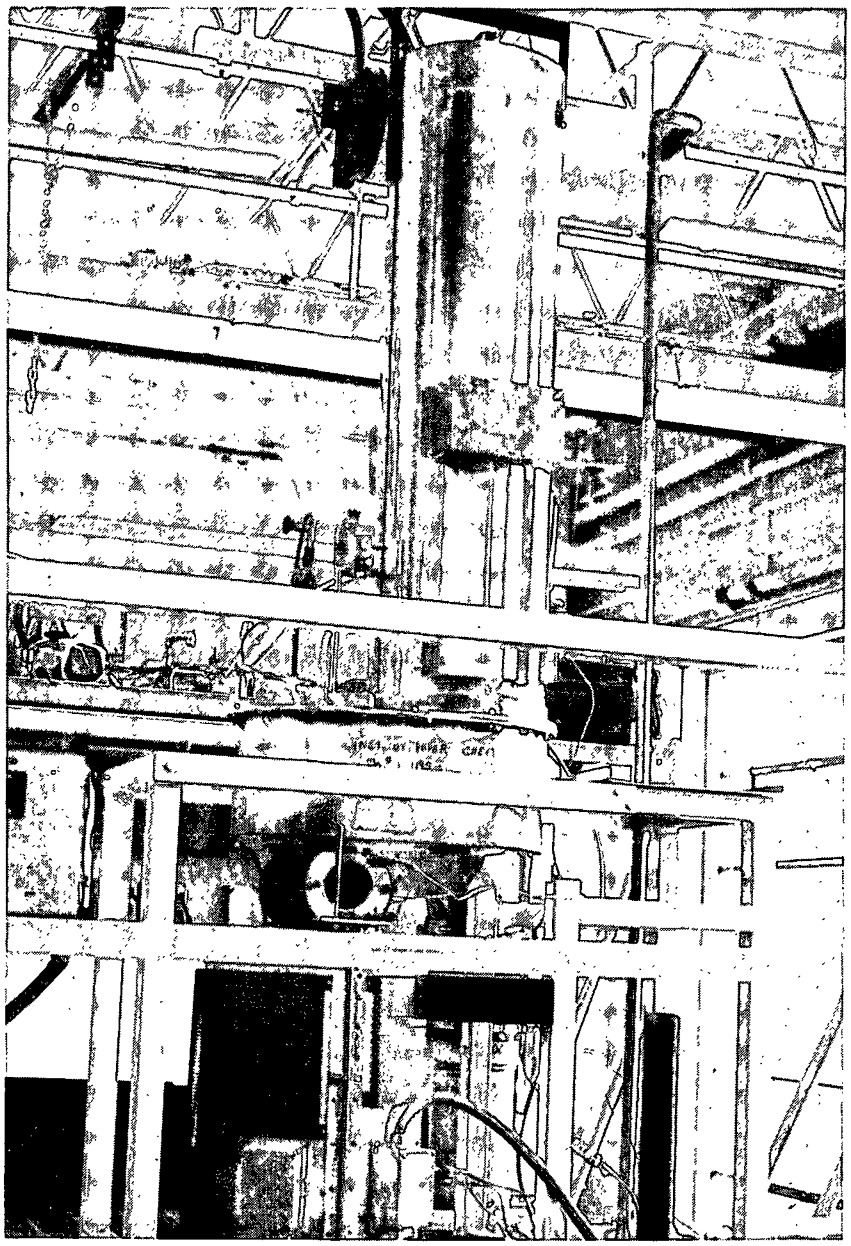
INSTALL AND BEGIN TESTING THE BED BURNING FURNACE.

COMPLETE DYNAMIC IN-FLIGHT TESTS.

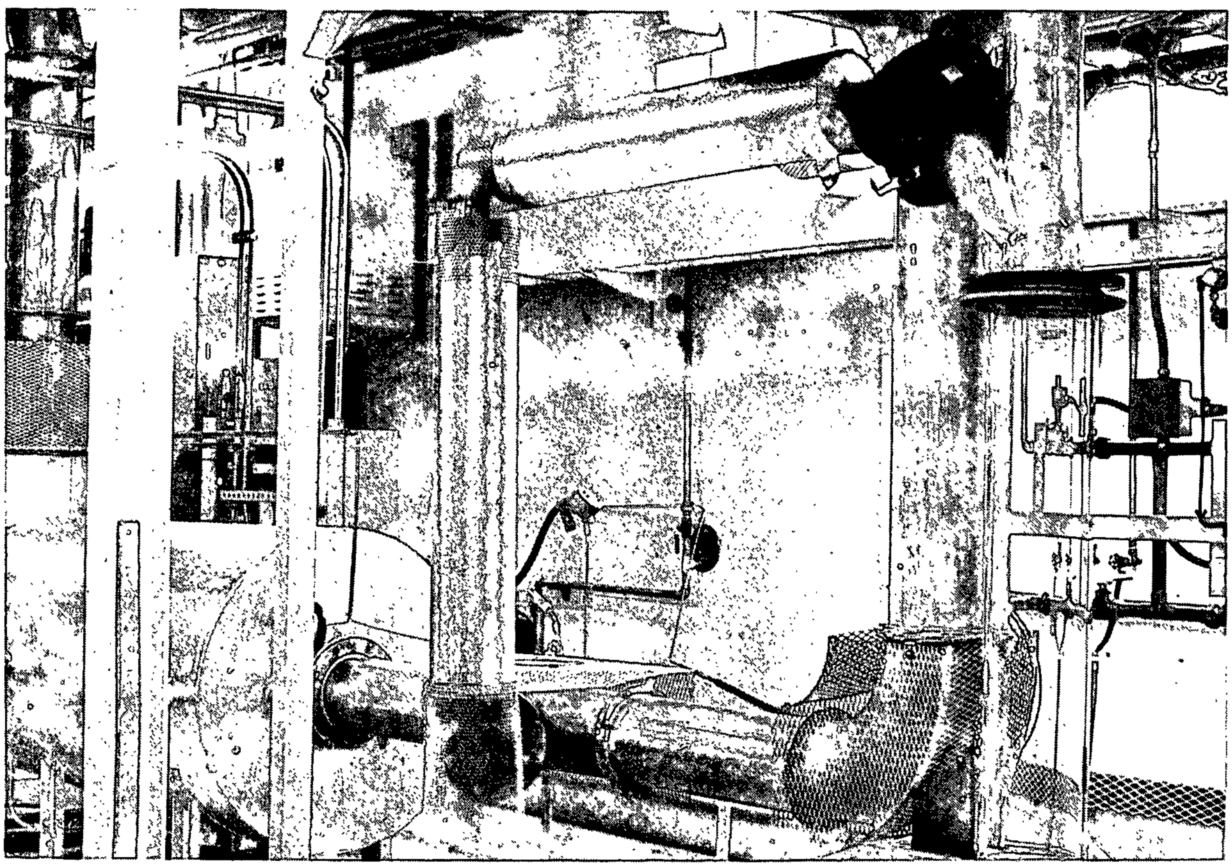
DESIGN NONINTRUSIVE BED BURNING MEASUREMENT STUDIES.



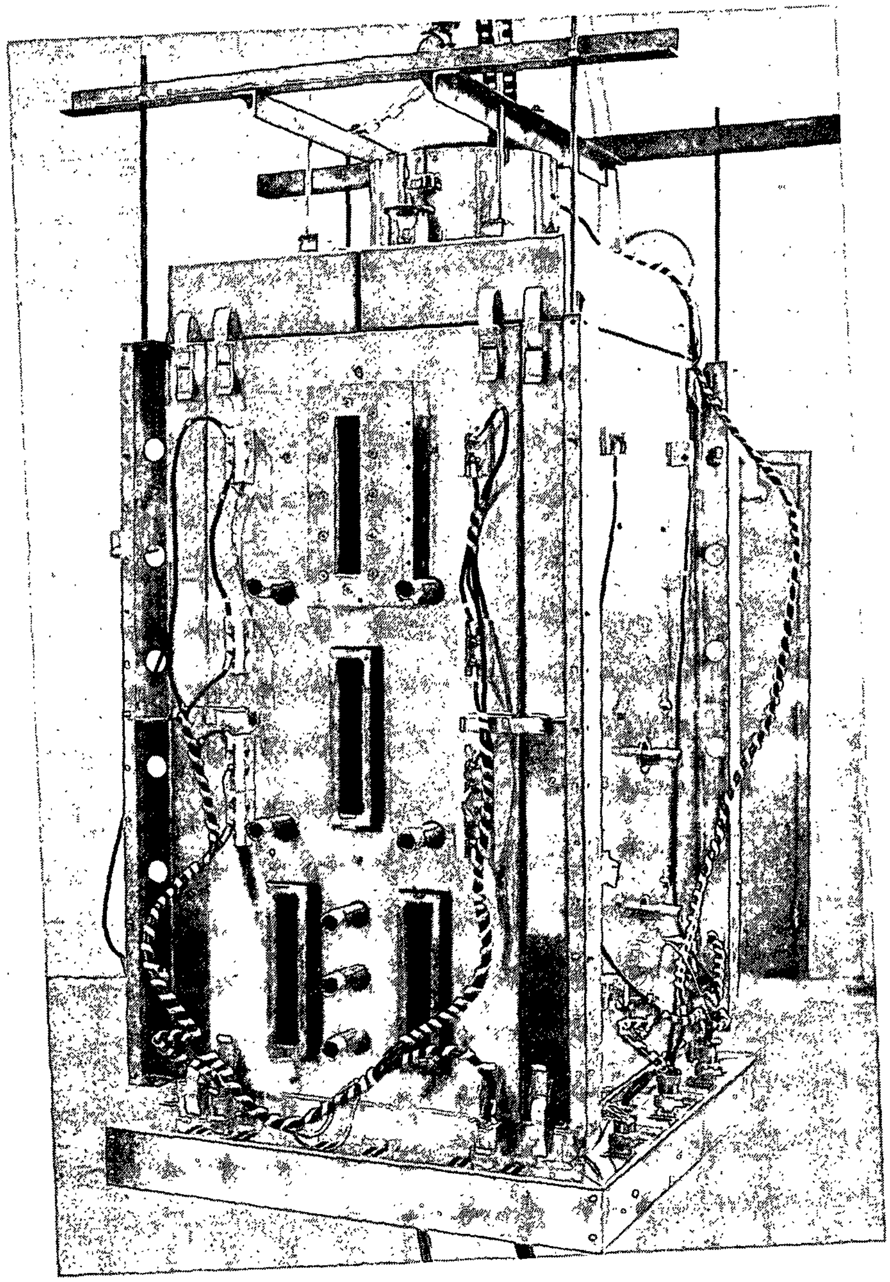
Down Flow Configuration of Black Liquor Flow Reactor.



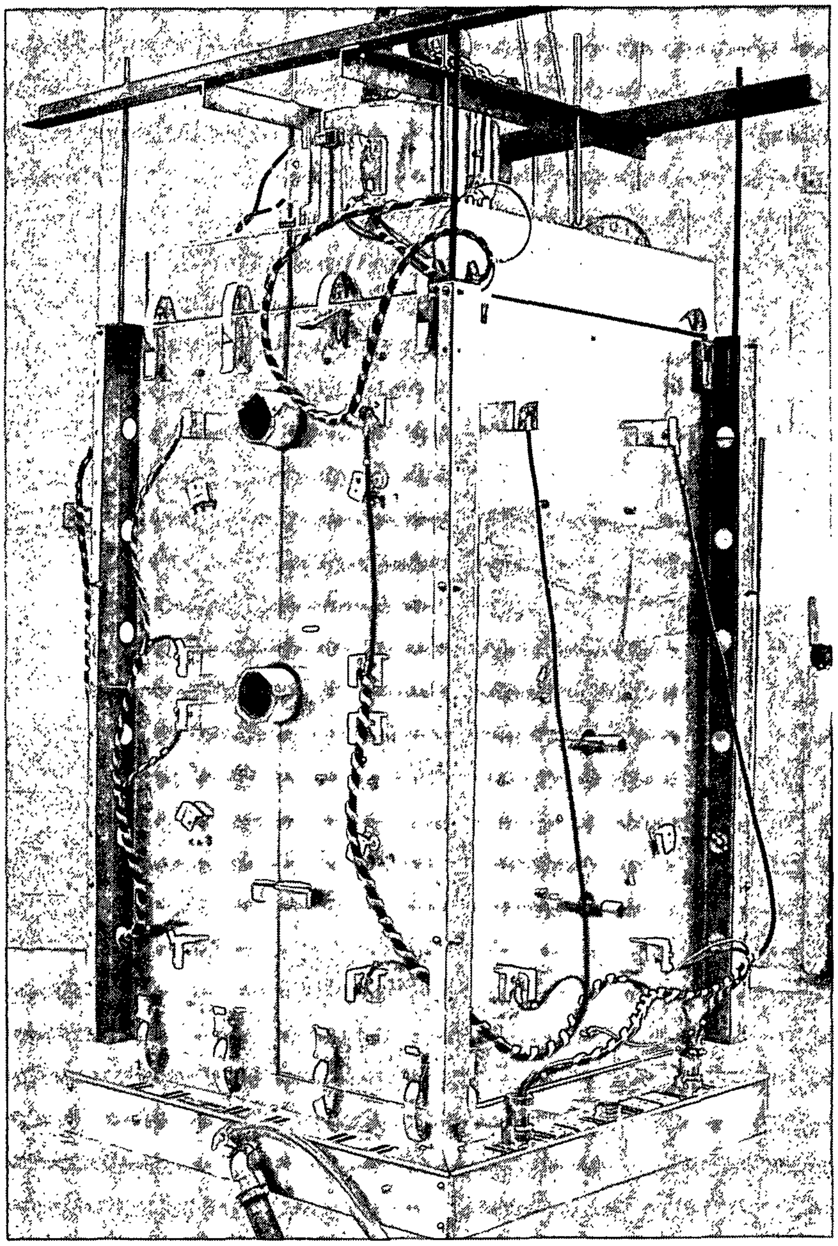
Preheater and Final Heater for Gas Stream in Down Flow System.



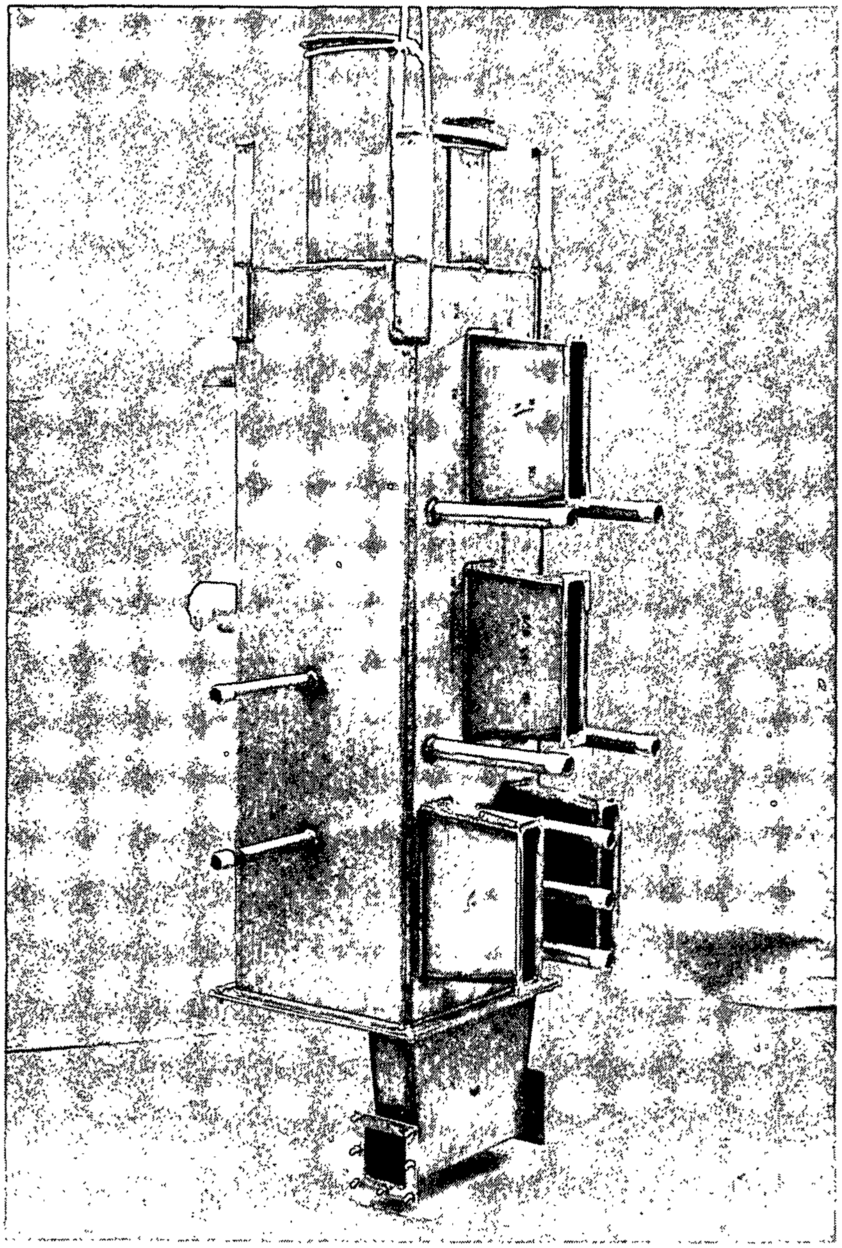
Char Collection in the Down Flow Configuration.



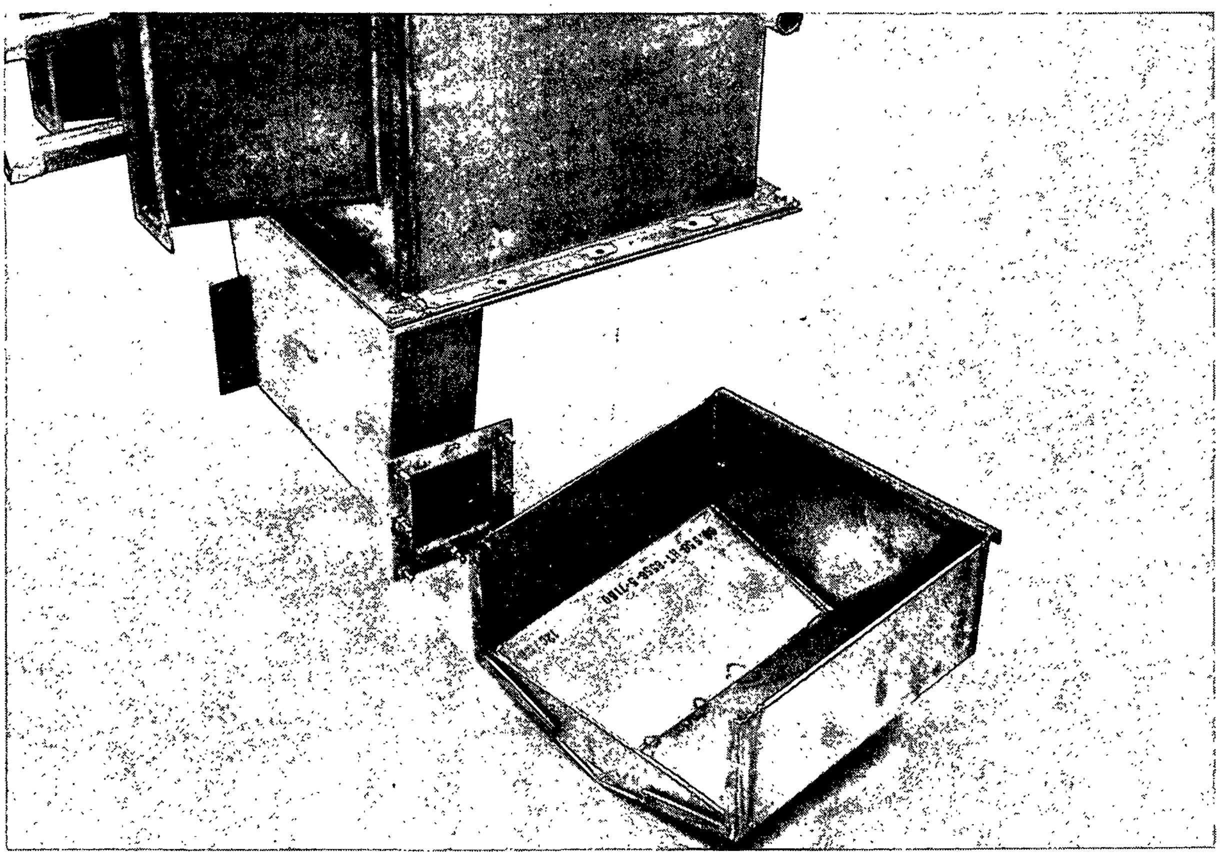
Char Bed System with Heaters, Front.



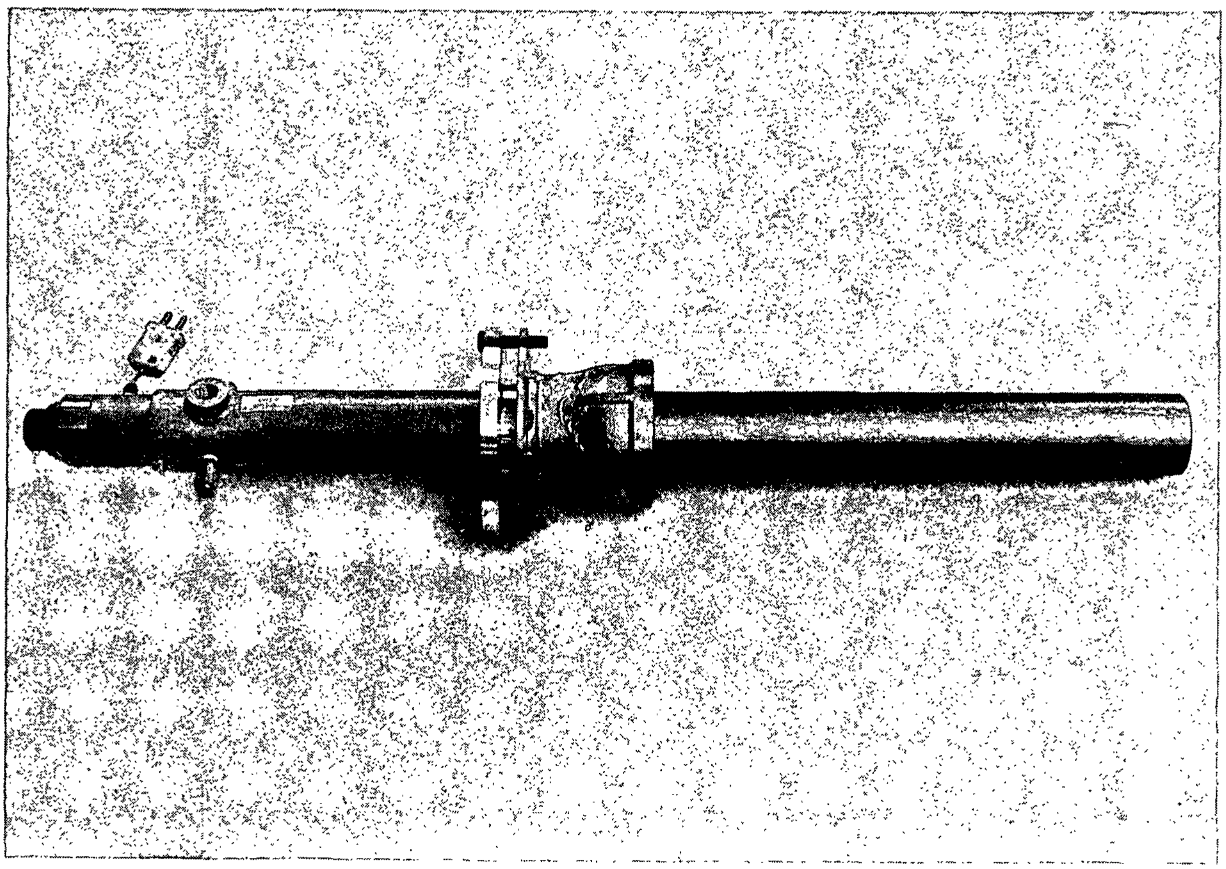
Char Bed System with Heaters, Back.



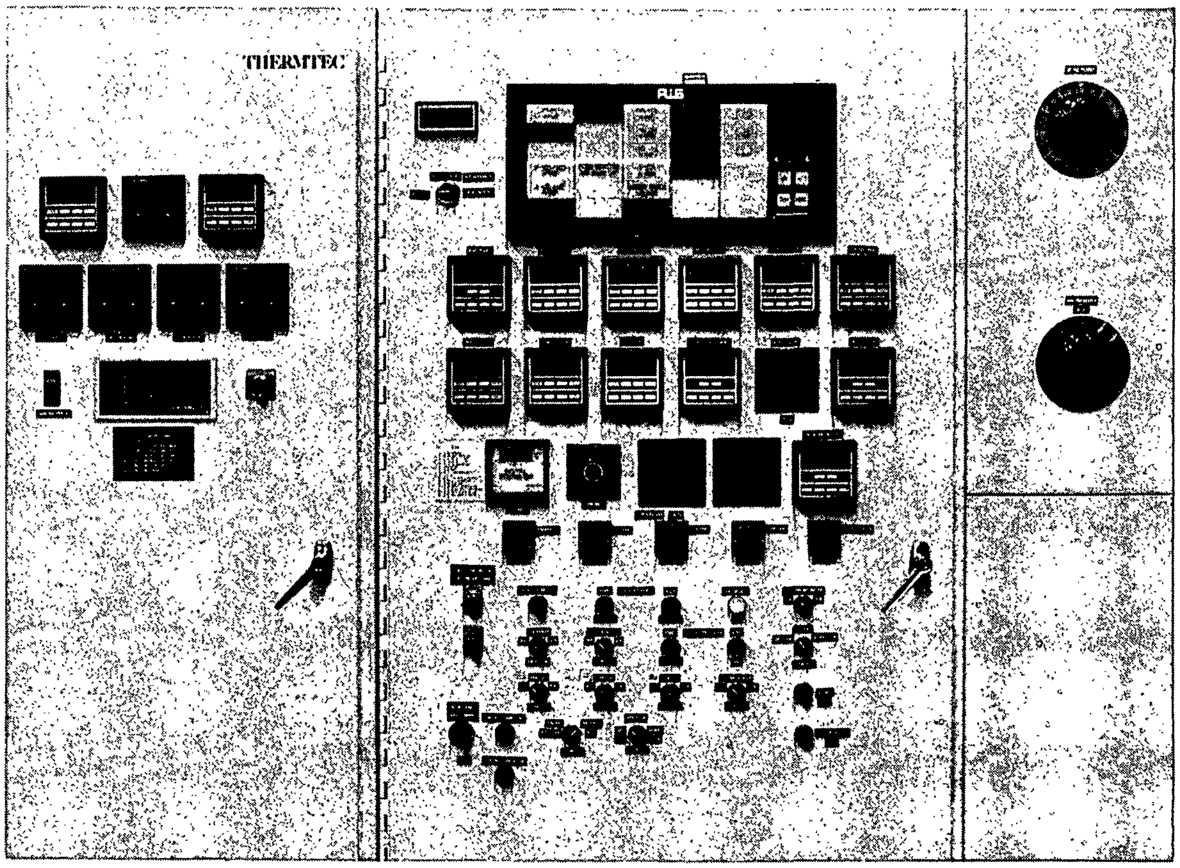
Metal Retort for Char Bed System.



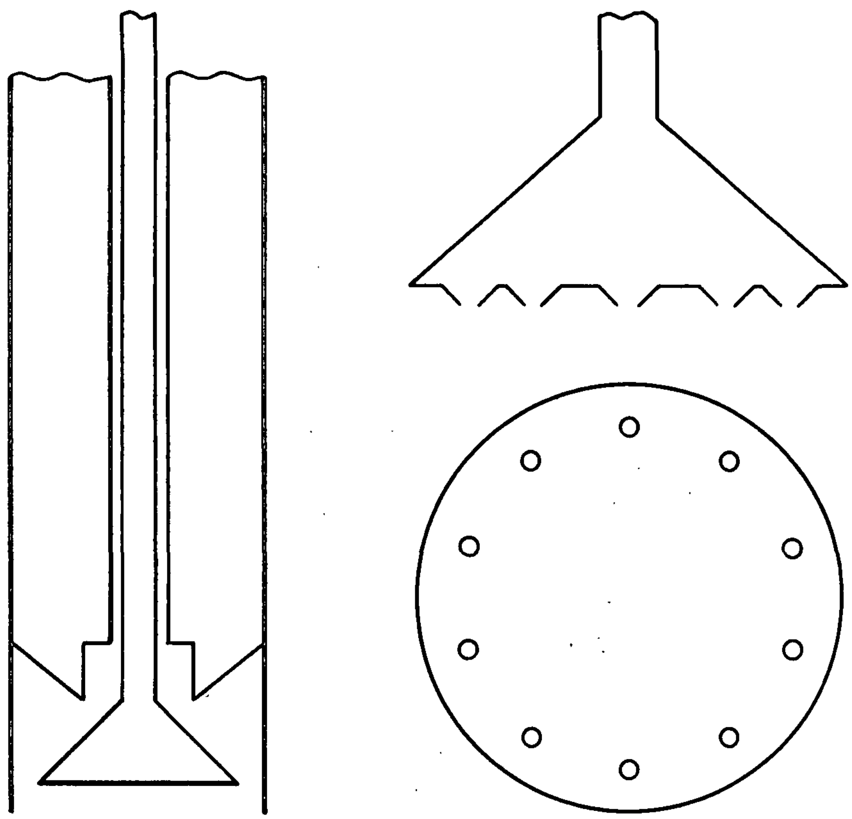
Char Bed Tray.



Boroscope for Char Bed System.



Black Liquor Flow Reactor Control Panel, Modified
for Down Flow and Char Bed Systems.



MULTIPLE PORT BLACK LIQUOR DROPLET INJECTOR

Recovery Overview

Tom Grace

BASIC BLACK LIQUOR BURNING FUNDAMENTALS

SINGLE PARTICLE COMBUSTION
STATUS OF KNOWLEDGE

	NOW	END 88
DRYING	80%	95%
VOLATILES BURNING		
VOLATILES PRODUCTION	60%	90%
SULFUR RELEASE	40%	85%
SWELLING	60%	70%
VOLATILES COMBUSTION	80%	95%
CHAR BURNING		
CARBON BURNUP	75%	95%
CO/CO_2 RATIO	50%	90%
FUME PRODUCTION RATES	35%	70%
SULFATE REDUCTION	90%	95%
SMELT COALESCENCE/OXIDATION		
SOLID-LIQUID TRANSFORMATION	35%	80%
REOXIDATION RATES	90%	95%
ROMAN CANDLE EFFECT	30%	80%
FUME PRODUCTION RATES	70%	90%
SEQUENCING OF STEPS	50%	90%

BURNING ON THE MACROSCALE

IN-FLIGHT PROCESSES
- DATA FROM DOE REACTOR (SO FAR ONLY FOR LARGE DROPS)
- MODELLING OF BEHAVIOR IN THE FURNACE (JUST STARTED)
- FURNACE AIR/GAS FLOW PATTERNS (USING B&W COLD FLOW DATA)
- SPRAY NOZZLE CHARACTERIZATION (FARRINGTON - JUST STARTING)

BED BURNING
- DATA ON BED BURNING RATES (JUST STARTING)
- MODELING OF BED BURNING RATES (JUST STARTING)

CARRYOVER/FUME PRODUCTION
- MODELLING TO PREDICT CARRYOVER (JUST STARTING)
- MODELLING OF FUME PRODUCTION (JUST STARTING)
- EXPERIMENTAL DATA FROM DOE REACTOR (PLANNED FOR 1988)

FOULING/PLUGGING
- DATA OF TRAN <u>ET AL</u>. (EXCELLENT START - NEEDS INTERPRETATION)
- EXPERIMENTAL DATA FROM DOE REACTOR (PLANNED FOR 1988)
- FUNDAMENTAL FUME DEPOSITION DATA (JUST STARTING)

SHORT TERM PLANS

(THROUGH CALENDAR YEAR 1988)

WORK ALREADY IN THE PIPELINE
- DOE PROJECT RUNS TO OCTOBER 1988
- MOST THESIS WORK WILL FINISH LATE 88/EARLY 89
- HUPA COLLABORATION
- FUNDAMENTAL SMELT CHEMISTRY
- SPRAY CHARACTERIZATION (TED FARRINGTON)

INITIATE WORK AIMED AT GASIFIERS
- 1-DIMENSIONAL MODELLING OF BLACK LIQUOR GASIFICATION
- EXPERIMENTAL IN-FLIGHT/CHAR-BURNING DATA FOR SMALL PARTICLES

TRY TO ESTABLISH A FORMAL TIE TO ACERC

PREPARE EDUCATIONAL MATERIALS ON BLACK LIQUOR COMBUSTION

MID-TERM PLANS

(THROUGH CALENDAR YEAR 1990)

WRAP UP FUNDAMENTAL WORK ON BLACK LIQUOR COMBUSTION

FOCUS ON APPLICATION TO EXISTING RECOVERY BOILERS
- METHODOLOGY FOR RETROFITTING EXISTING UNITS
  - IMPROVED SPRAYS
  - OPTIMAL AIR/LIQUOR INJECTION SYSTEMS
- QUANTITATIVE ASSESSMENT OF PLUGGING BEHAVIOR
- DEVELOP ADVANCED SENSORS

FOCUS ON APPLICATION TO GASIFIERS
- COOPERATE WITH MOLTEN SALT GASIFICATION WORK
- COOPERATE WITH CYCLONE GASIFIER DEVELOPMENTS

EXPLORE FIRING OF VERY-HIGH/DRY SOLIDS LIQUOR
- EXPERIMENTAL DATA ON DOE REACTOR
- USE FURNACE MODEL TO EXPLORE BURNING BEHAVIOR
- WORK ON DRY SOLIDS PRODUCTION TECHNIQUES

LONG RANGE PLANS

(BEYOND 1990)
(POSSIBILITIES ONLY)

RECOVERY TECHNOLOGIES FOR HIGH-YIELD PULPING PROCESSES
EXPAND INTO FUNDAMENTALS OF ASH BEHAVIOR IN GENERAL
DEVELOP DRY SOLIDS TECHNOLOGY
SO_2 REMOVAL FROM STACK GASES

Project 3475

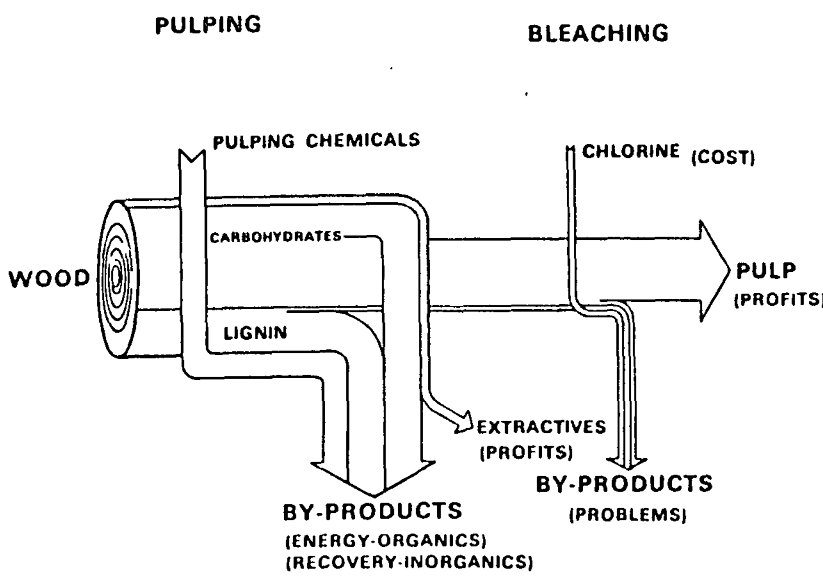
Don Dimmel

PROJECT 3475

FUNDAMENTALS OF SELECTIVITY
IN PULPING AND BLEACHING

DELIGNIFICATION REACTIONS

CARBOHYDRATE REACTIONS



PULPING MATERIAL BALANCES

OBJECTIVES
PROJECT 3475

Develope a fundamental understanding of
the chemical and physical reactions
that control
degradation rates and structural changes of
lignin, cellulose, and hemicelluloses
during
pulping and bleaching

PULPING CHEMISTRY

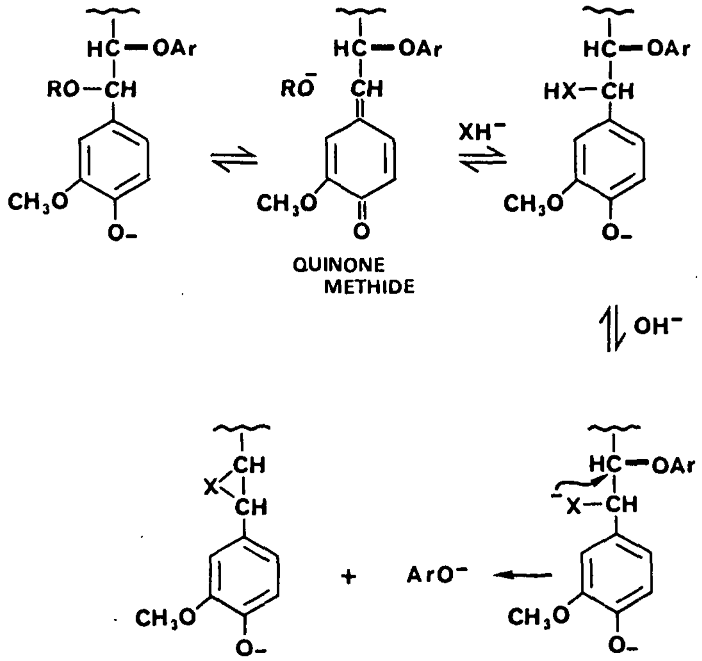
STUDENT RESEARCH ⇌ **PROJECT RESEARCH**

STUDENT RESEARCH
- PEGGY SANDS (MS)
- PATRICK MEDVECZ (MS)
- JOSEPH LEEGE (MS)
- MATTHEW BOVEE (Ph.D.)

- PATRICK APFELD (Ph.D.)
- MARGARET HENDERSON (Ph.D.)
- DEAN SMITH (Ph.D.)

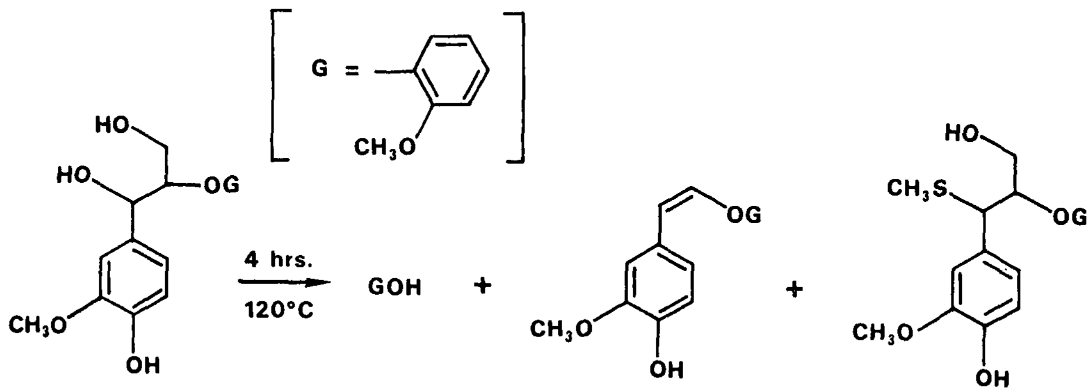
PROJECT RESEARCH
- LOIS SCHULLER (BS)
- HOLLY LINGNOWSKI (BS)

CLEAVAGE OF C_{β}-O_4 ETHER BONDS



where X = O or S

DELIGNIFICATION BY METHYL MERCAPTAN

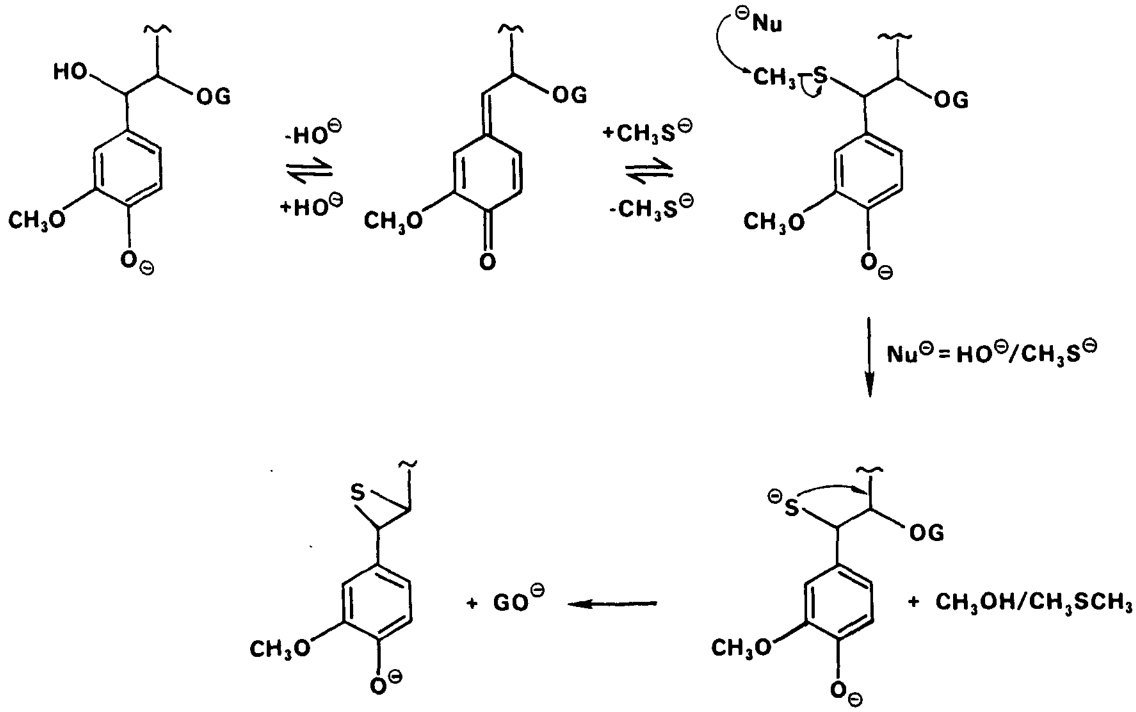


30%	NaOH	15%	32%	–
18%	NaOH $NaSCH_3$	26%	4%	20%

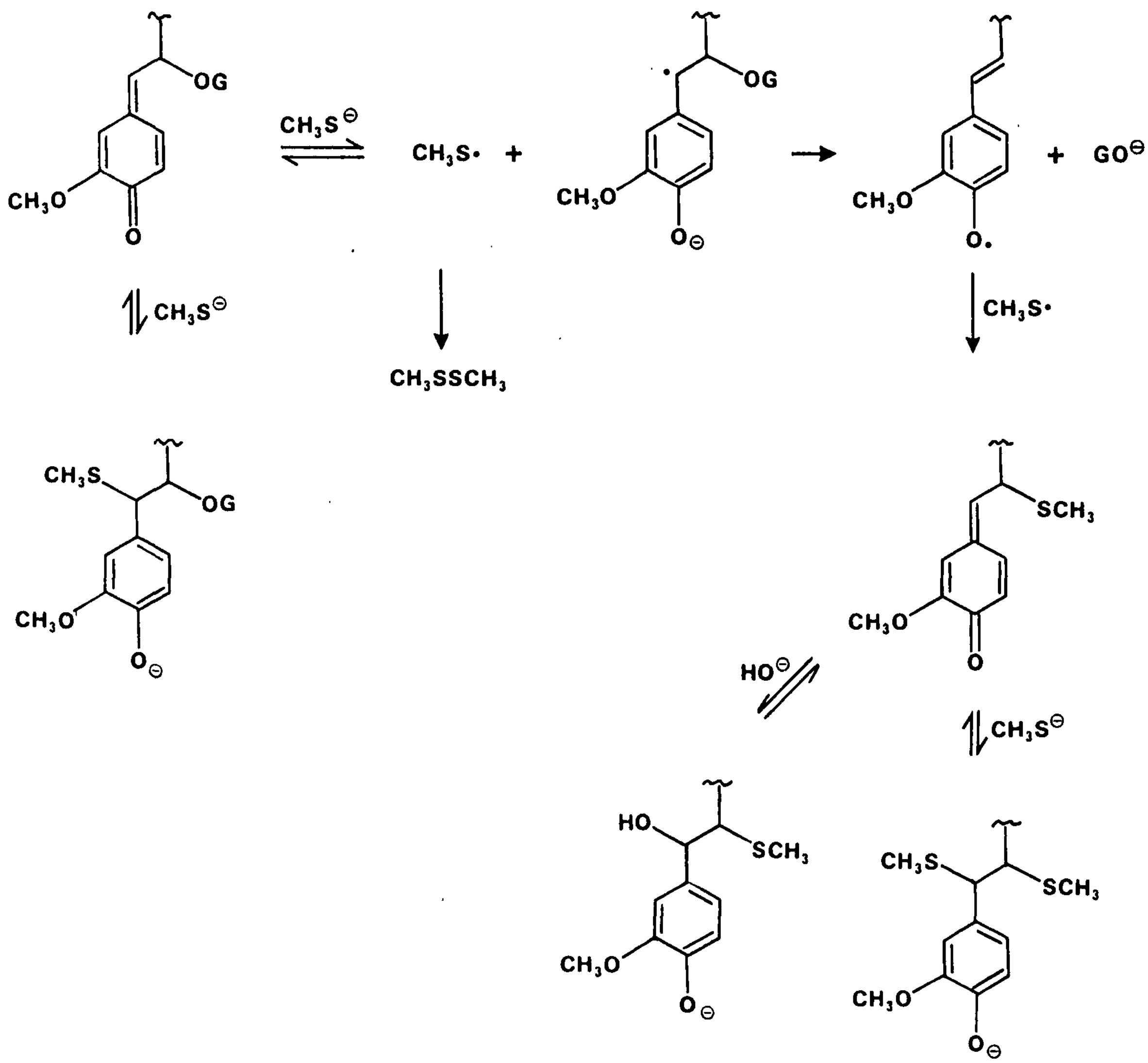
Ohara, Meshitsuka, and Nakano, J. Japan. Wood Res. Soc., 1983, 29, 611

POSSIBLE METHYL MENCAPTAN DELIGNIFICATION MECHANISM
IONIC NUCLEOPHILLIC DISPLACEMENT

PEGGY SANDS

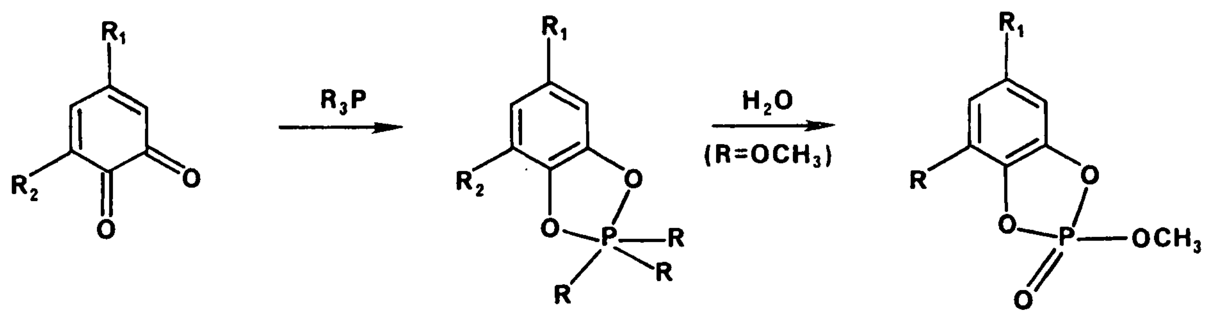


POSSIBLE METHYL MERCAPTAN DELIGNIFICATION MECHANISM
ELECTRON TRANSFER



REACTIONS OF TRIVALENT PHOSPHOROUS COMPOUNDS WITH ORTHO QUINONES

PAT MEDVECZ

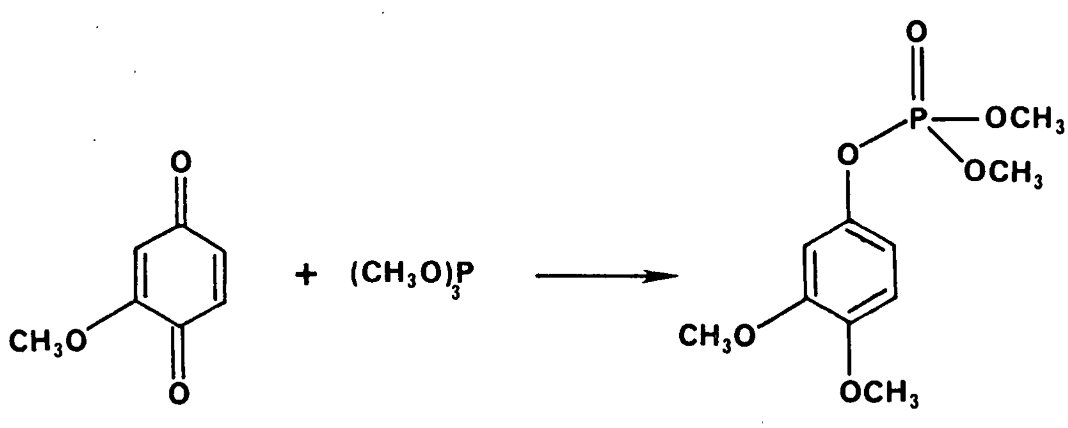


$R_1 = R_2 =$ t-BUTYL

$R_1 = H,\ R_2 = OCH_3$

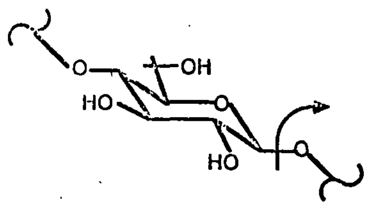
REACTIONS OF TRIVALENT PHOSPHOROUS COMPOUNDS WITH PARA QUINONES

PAT MEDVECZ

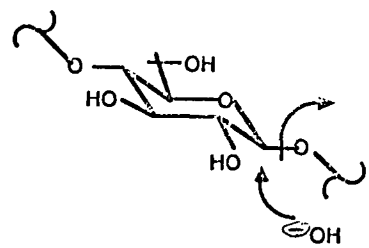


Glycosyl-Oxygen Bond

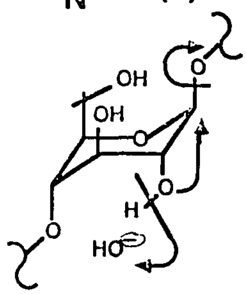
S_N1



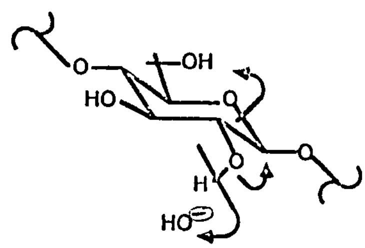
S_N2



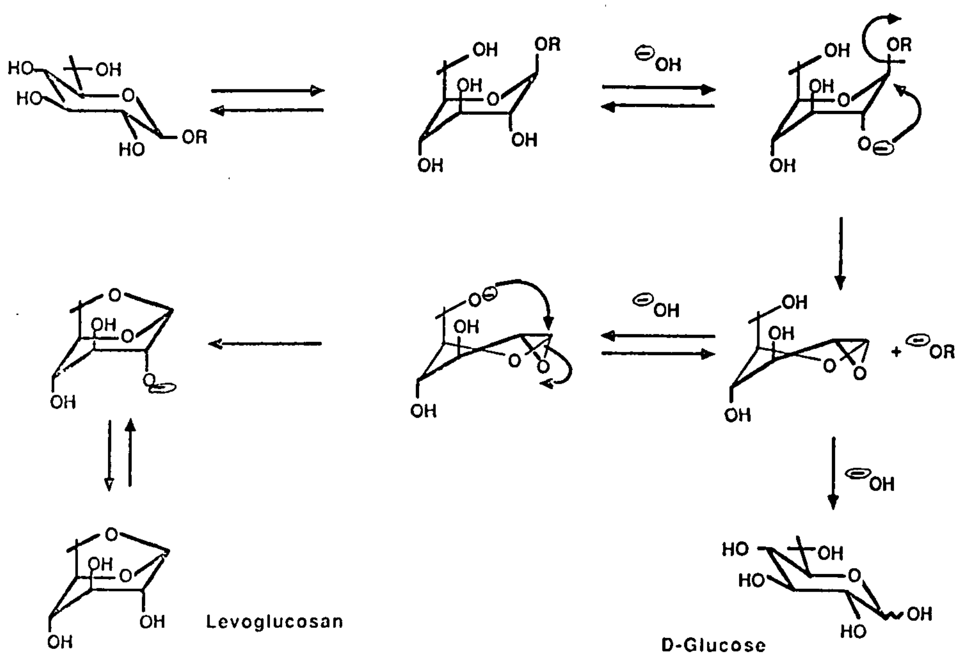
$S_N1cB(2)$



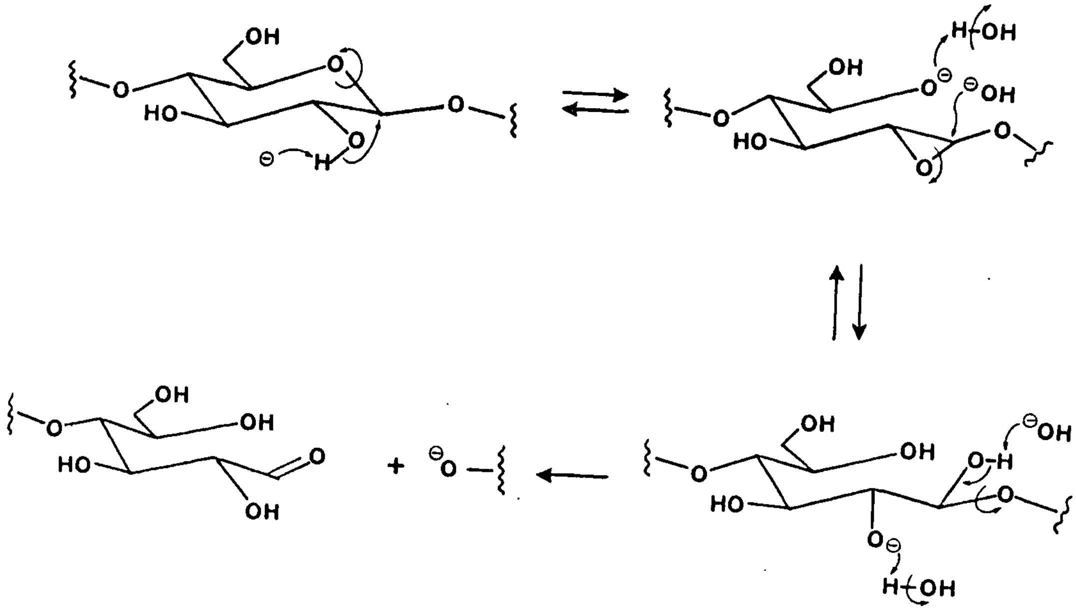
$S_N1cB(2ro)$



$S_N1cB(2)$

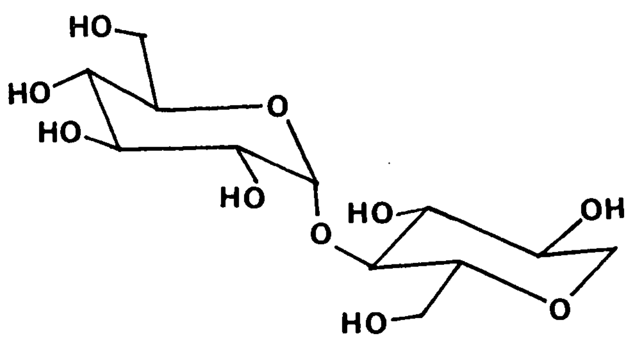


S_N1cB (2) - ro



SODIUM HYDROXIDE DEGRADATION REACTIONS OF 1,5-ANHYDROMALTITOL

JOE LEEGE



Degradations done at

200°

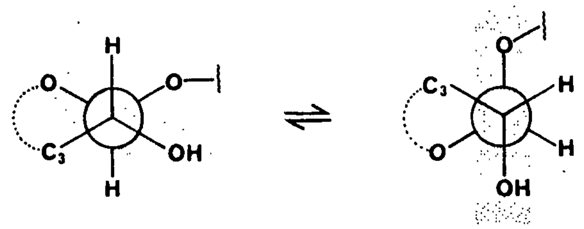
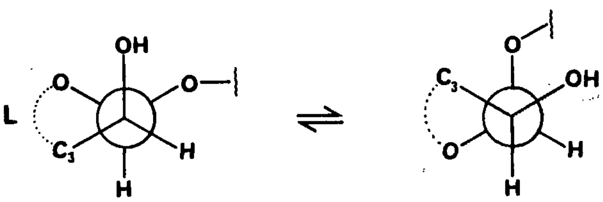
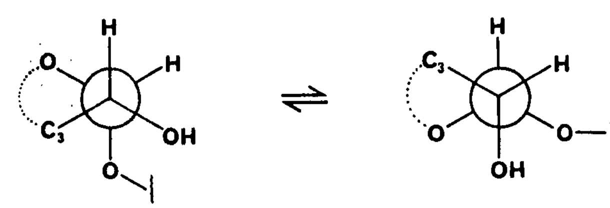
190°

180°

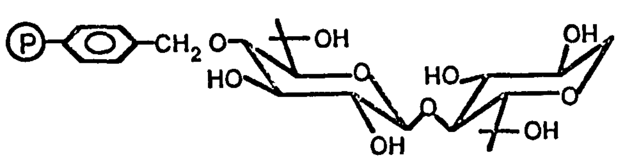
170°

$\Delta H^{\ddagger} = 36$ Kcal/mole $\Delta S^{\ddagger} = -6$ cal/mole-°K

NEWMAN PROJECTIONS FOR C_2-C_1 BONDS

CARBOHYDRATE (REL. RATE)	STABLE		UNSTABLE
1,5–ANHYDROCELLOBIITOL (8)			
1,5–ANHYDROMANNOBIITOL (4)			
1,5–ANHYDROMALTITOL (1)			

OBJECTIVE

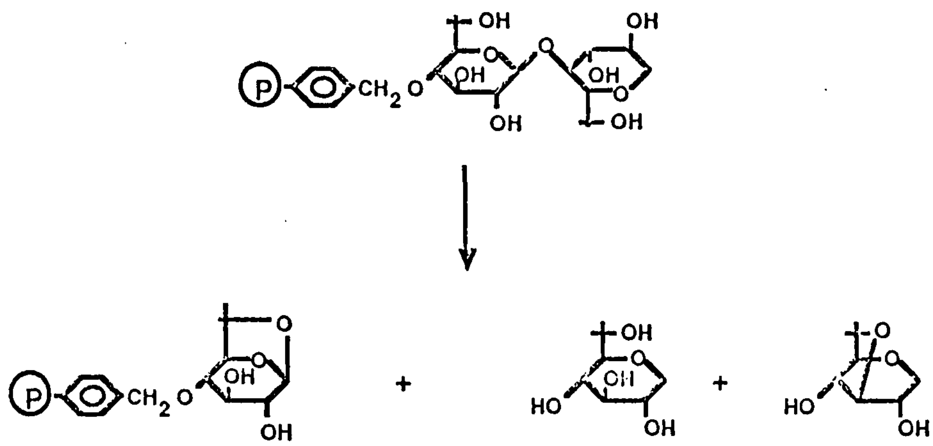


Ⓟ- polystyrene support

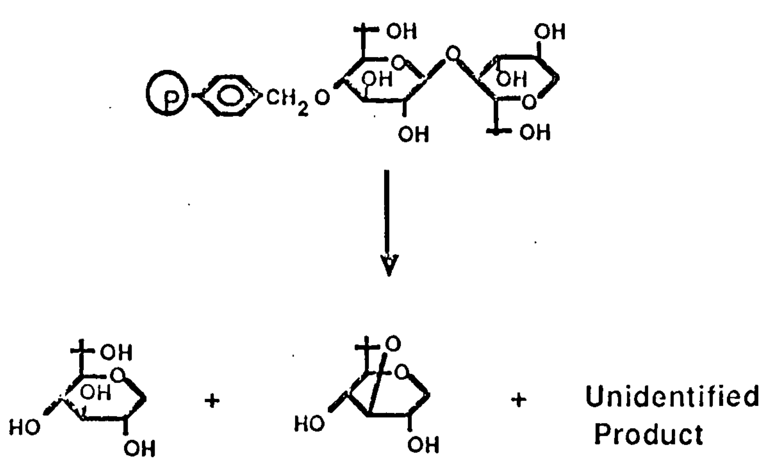
Synthesis

Reaction
- -rate
- -points of bond cleavage
- -mechanisms
- -products

Degradation

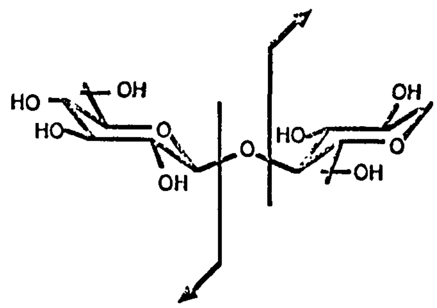


Degradation



Oxygen-aglycon bond

10-20%
S_N1
1,5:3,6-dianhydro-D-galactitol



Glycosyl-oxygen bond

80-90%
$S_N1cB(2)$

1,5-anhydro-D-glucitol
Levoglucosan

PREPARATION OF A HIGH VISCOSITY AMORPHOUS CELLULOSE

COTTON LINTERS

↓ DISSOLVE

REGENERATE, WASH

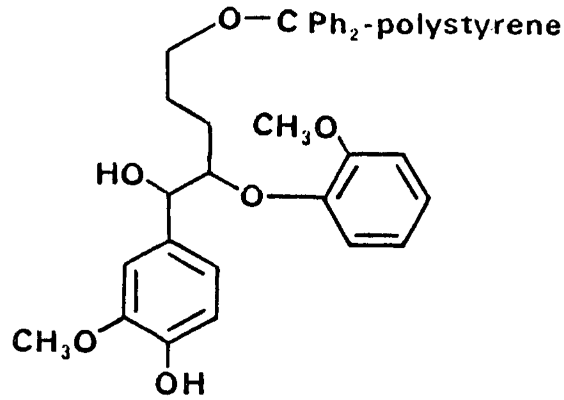
AMORPHOUS CELLULOSE		AMORPHOUS CELLULOSE	
UNTREATED	$NaBH_4$ REDUCED	$NaBH_4$ REDUCED	UNTREATED
VISC. = 2.3, 2.2	VISC. = 32.9, 33.4	VISC. = 29.1, 26.2	VISC. = 2.1, 2.1

ANOTHER AMORPHOUS CELLULOSE $\xrightarrow[\text{2 DAYS, 20°C}]{\text{1M NaOH}}$ VISC. = 32.5, 35.1

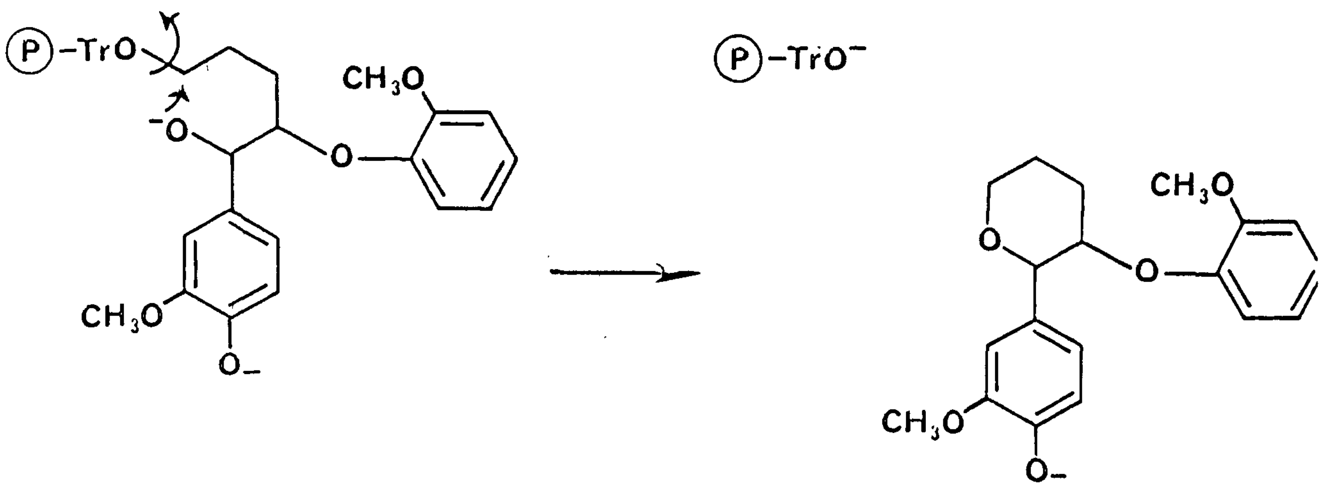
VISC. = 45.4, 47.3

SODA "PULPING" OF $NaBH_4$ REDUCED COTTON LINTERS WITH AND WITHOUT 1% AQ

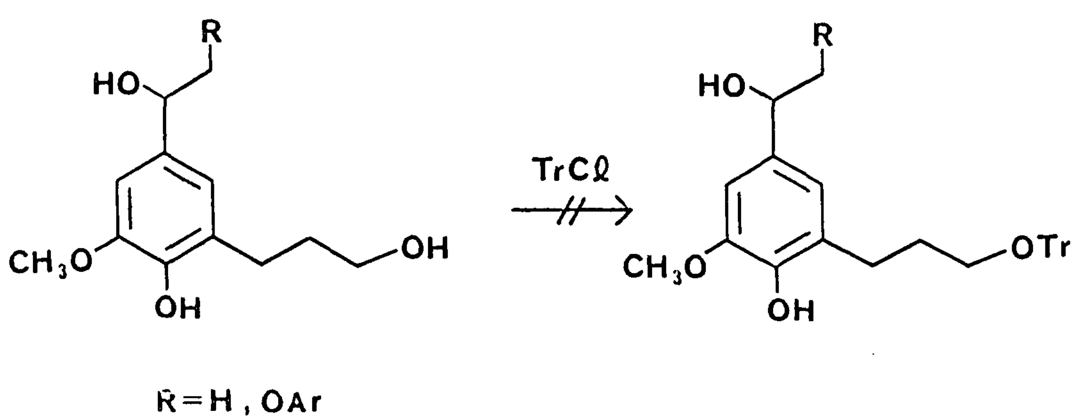
TIME (HRS) AT 170°C	AQ	VISCOSITY	TIME (HRS) AT 170°C	AQ	VISCOSITY
0	—	7.50, 7.47	0	✓	7.08, 7.09
0	—	7.35, 7.46	0	✓	7.09, 7.05
1	—	5.44, 5.41	1	✓	4.82, 4.88
1	—	5.50, 5.49	1	✓	4.88, 4.88
1	✓	5.20, 5.13	2	✓	3.84, 3.86
2	—	4.03, 4.07	2	✓	3.90, 3.90
2	—	4.32, 4.29			



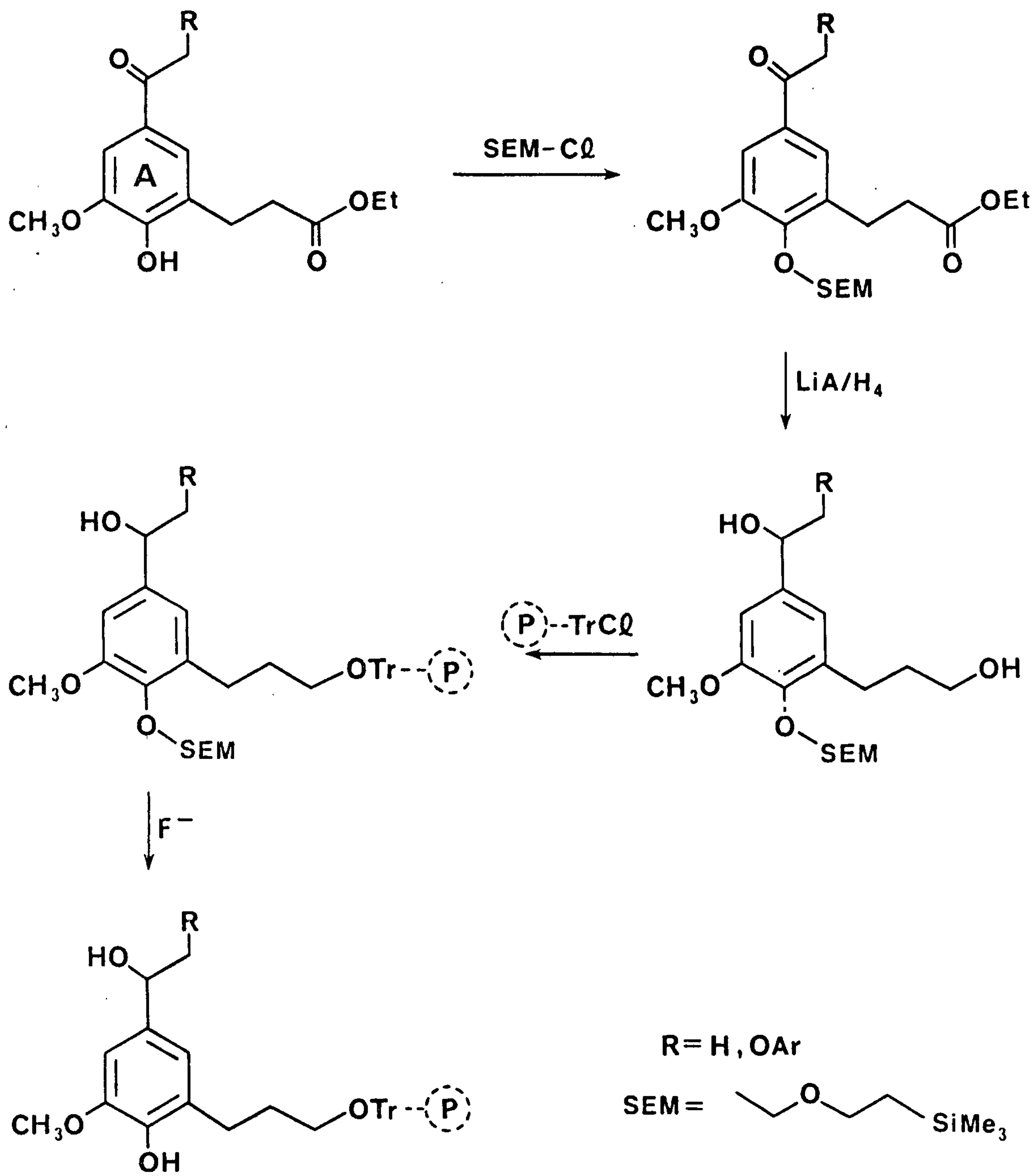
RELEASE OF MODEL FROM POLYMER



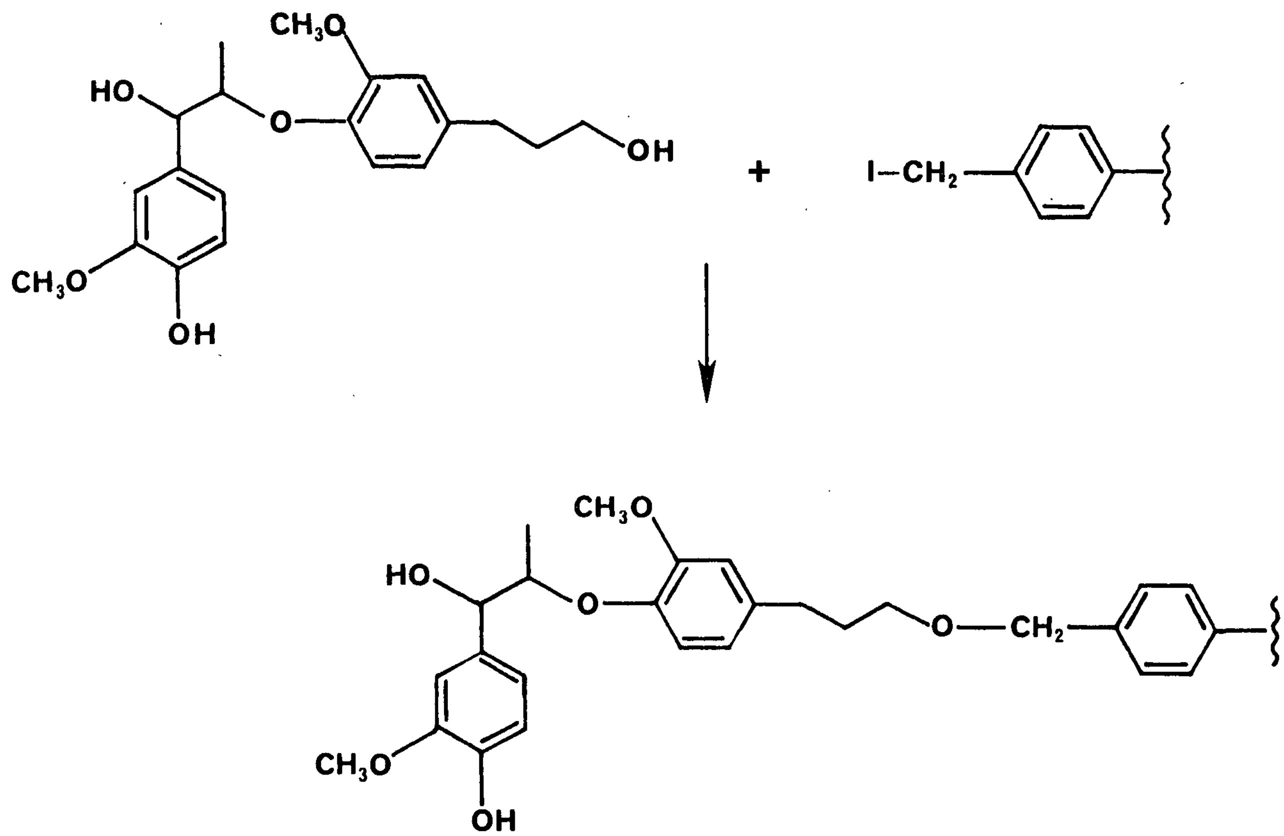
UNSUCCESSFUL TRITYLATION OF A-RING MODEL



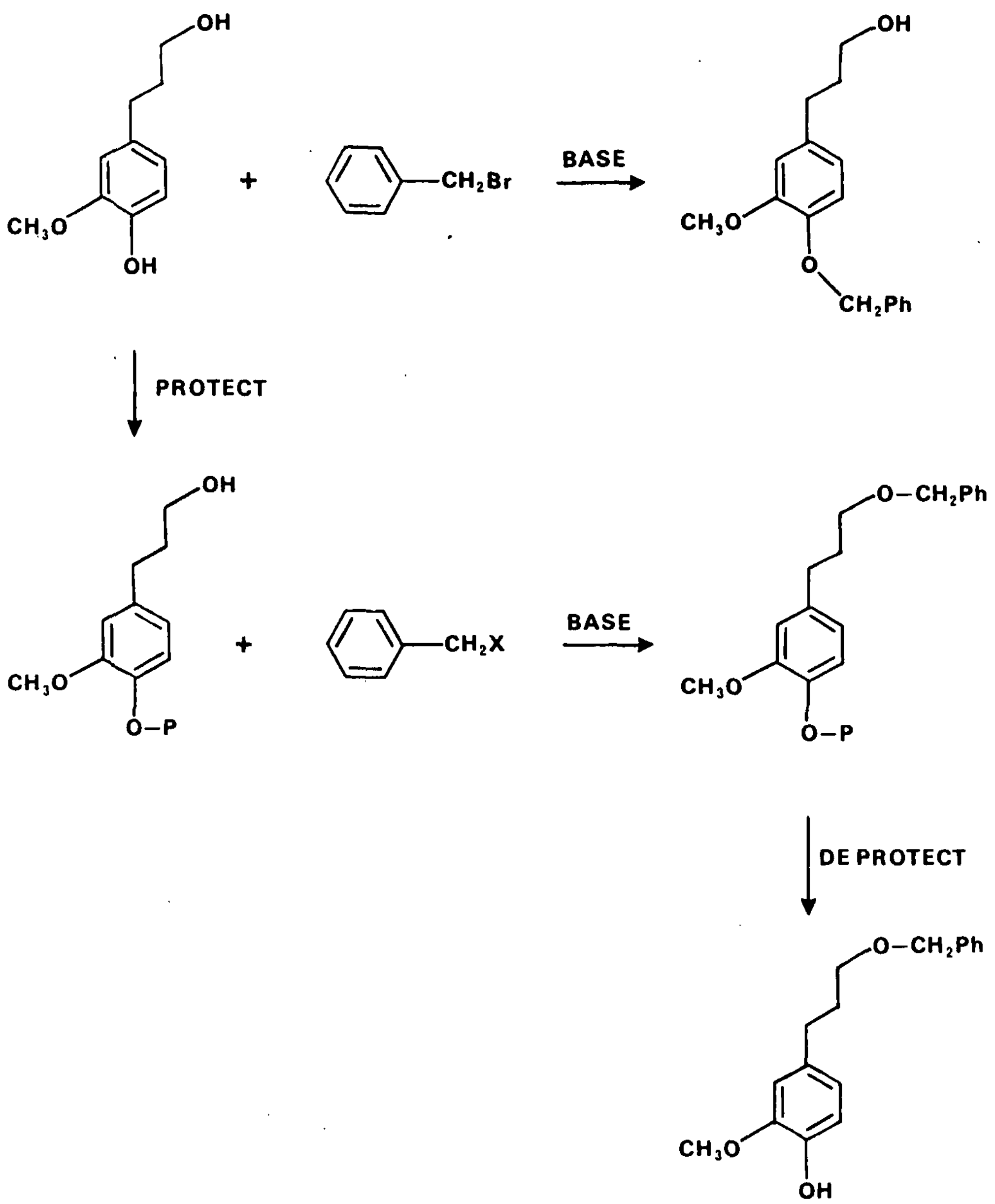
SYNTHETIC SCHEME FOR A-RING MODEL POLYMER ATTACHMENT



INSOLUBLE LIGNIN MODEL SYNTHESIS

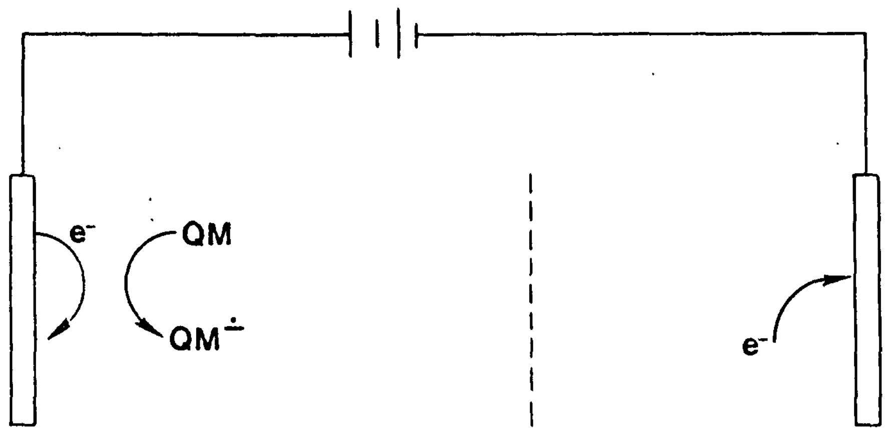


SYNTHETIC STUDIES LEADING TO INSOLUBLE LIGNIN MODELS

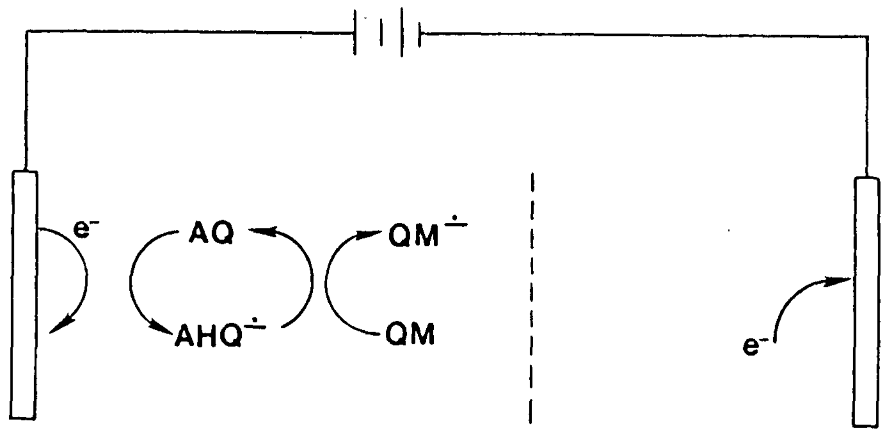


ELECTROCHEMICAL STUDIES

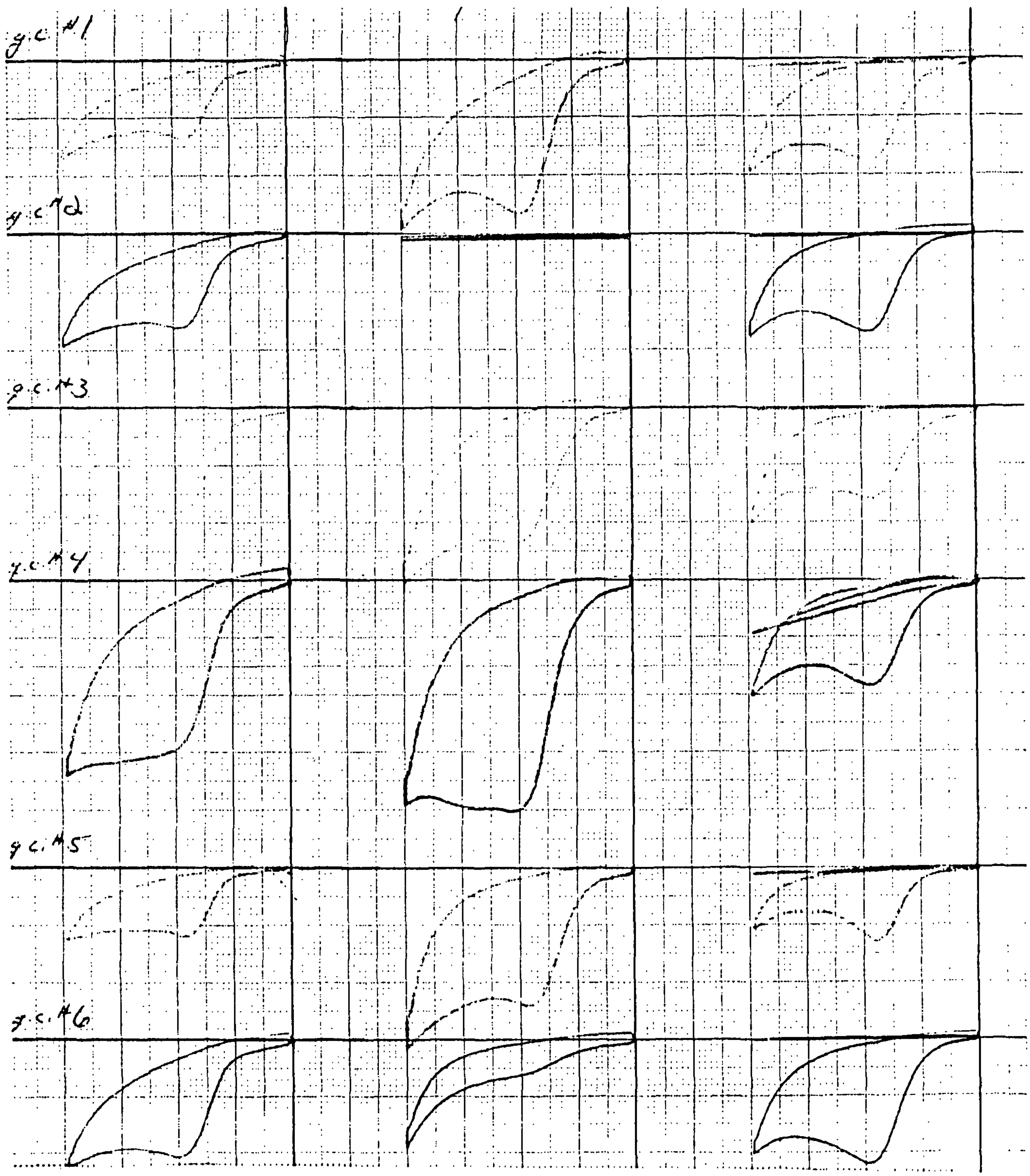
ELECTROCHEMISTRY AND PULPING

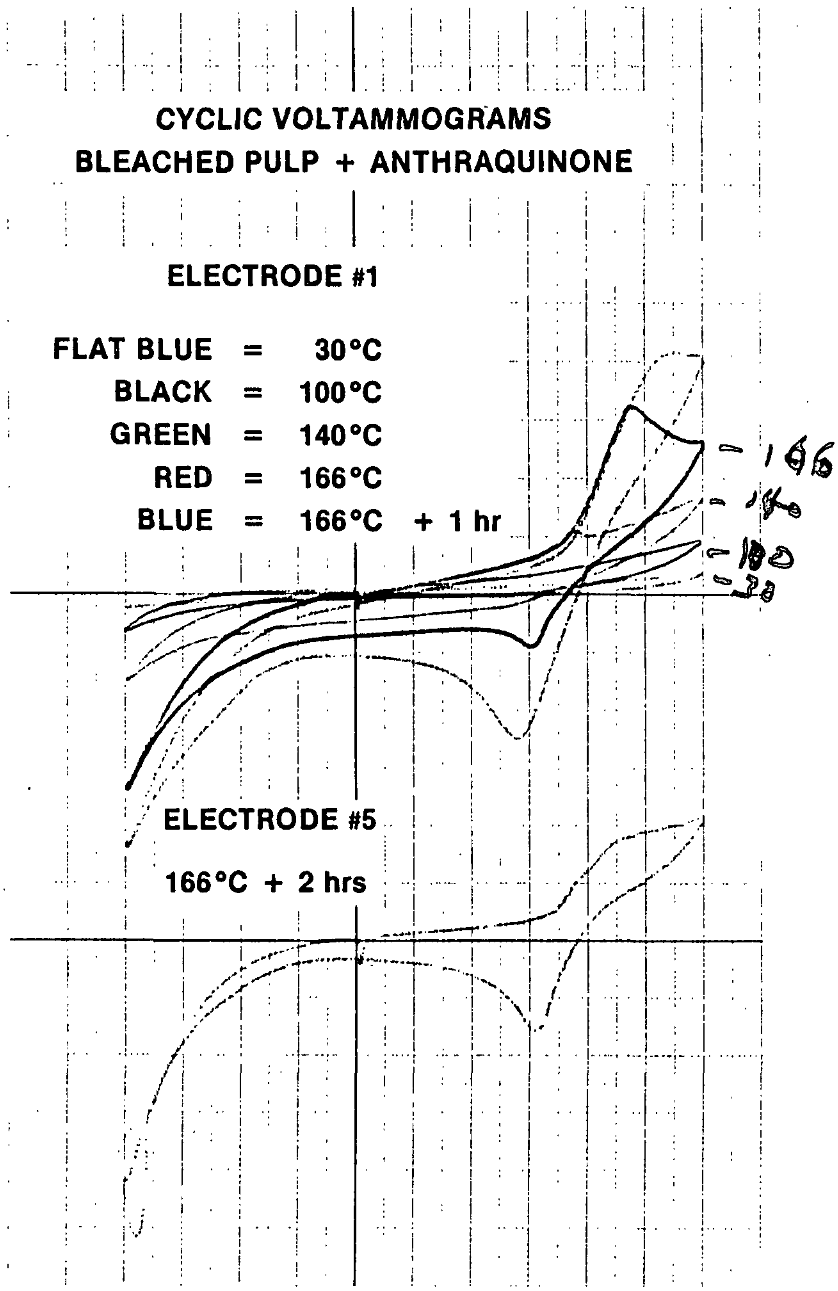


ELECTROCHEMISTRY AND PULPING



ELECTRODE CHECK

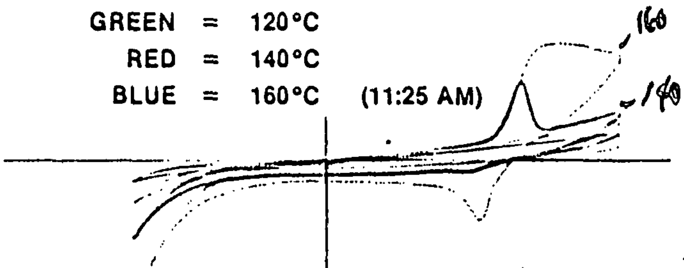


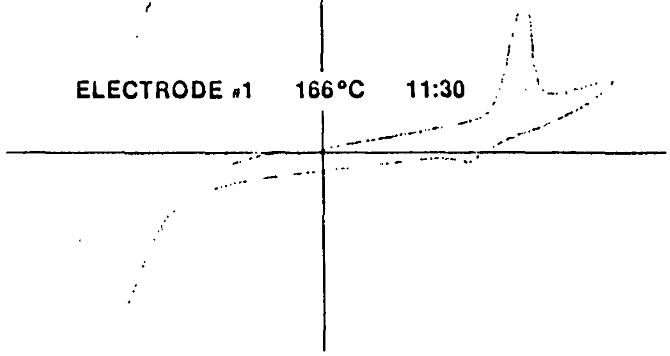

CYCLIC VOLTAMMOGRAMS
BLEACHED PULP + ANTHRAQUINONE
ELECTRODE #1
FLAT BLUE = 30°C
BLACK = 100°C
GREEN = 140°C
RED = 166°C
BLUE = 166°C + 1 hr
166
140
100
30
ELECTRODE #5
166°C + 2 hrs

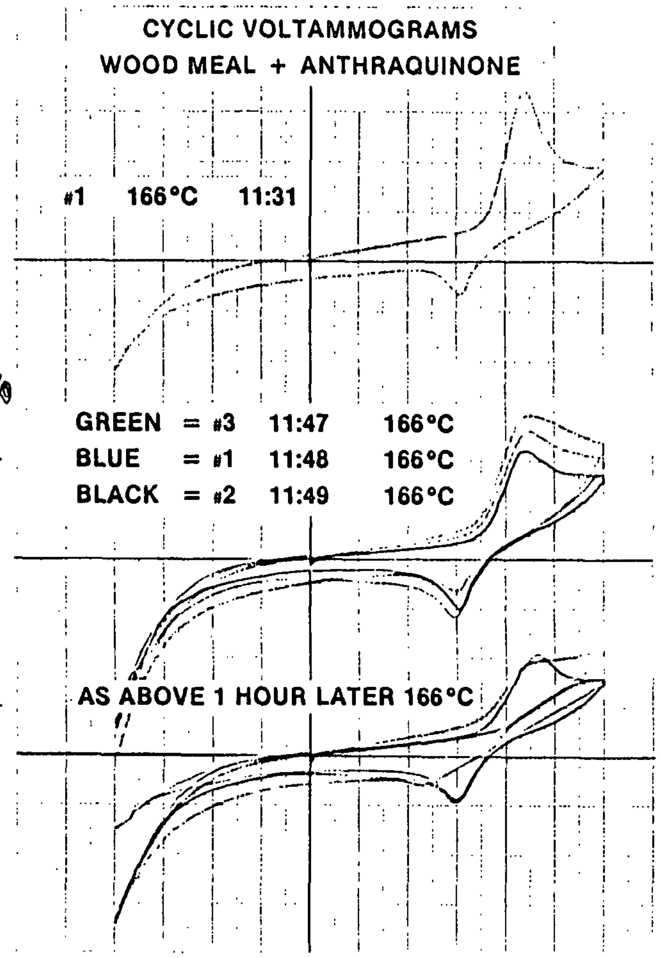
CYCLIC VOLTAMMOGRAMS
WOOD MEAL + ANTHRAQUINONE

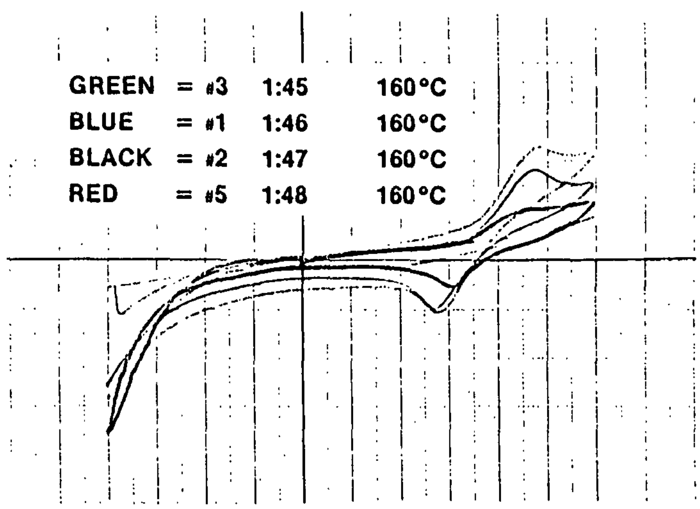
ELECTRODE #3

FLAT BLUE = 60°C
BLACK = 100°C
GREEN = 120°C
RED = 140°C
BLUE = 160°C (11:25 AM)









Project 3477

Dwight Easty

Pyrolysis Gas Chromatography: Identification of
Polymeric Additives and Contaminants in Paper

Samples received for identification by Analytical Sciences Group

About 1000 per year

Use of PGC: To complement FTIR.

Especially for unknowns which are

- nonvolatile
- crosslinked and insoluble
- small in amount
- indistinguishable from other materials via infrared

Features desired in pyrograms:

- characteristic of compound or class of compounds
- reproducible
- interpretable

Future Work

To improve interpretability of pyrograms:

- pyrolysis and GC conditions
- sequential pyrolysis
- "external pyrolysis"
- identification via characteristic ions (mass spectrometer)

Expand library of pyrograms

Test with "unknowns"

The Analysis of Polymers in Paper
by Pyrolysis Gas Chromatography

Thomas D. Crockett, M.S., IPC, 1987

State of the art prior to this investigation:

- limited work on PGC of polymers in paper matrix
- evidence that cellulose is more easily pyrolyzed than other polymers
- pyrolysis products should be identifiable by MS
- PGC shows promise as a quantitative technique

Objective

Develop a PGC method to characterize polymeric additives directly in paper matrix.

Steps in Investigation

Develop pyrolysis conditions to minimize paper contribution to pyrograms.

Develop GC conditions to produce characteristic pyrograms.

Establish a library of pyrograms.

Identify main pyrolysis products by mass spectrometry.

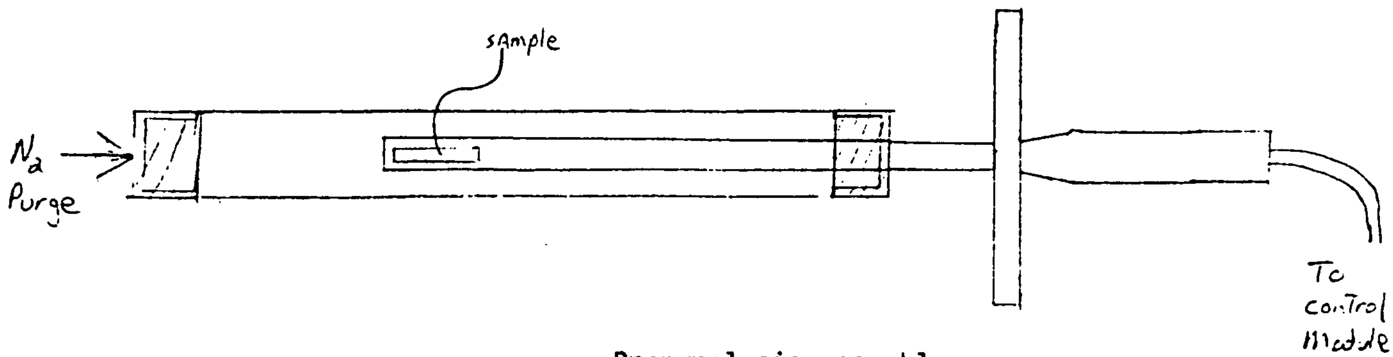
Qual. and quant. analysis of paper containing known added polymers.

Test the procedure by analysis of commercially produced papers.

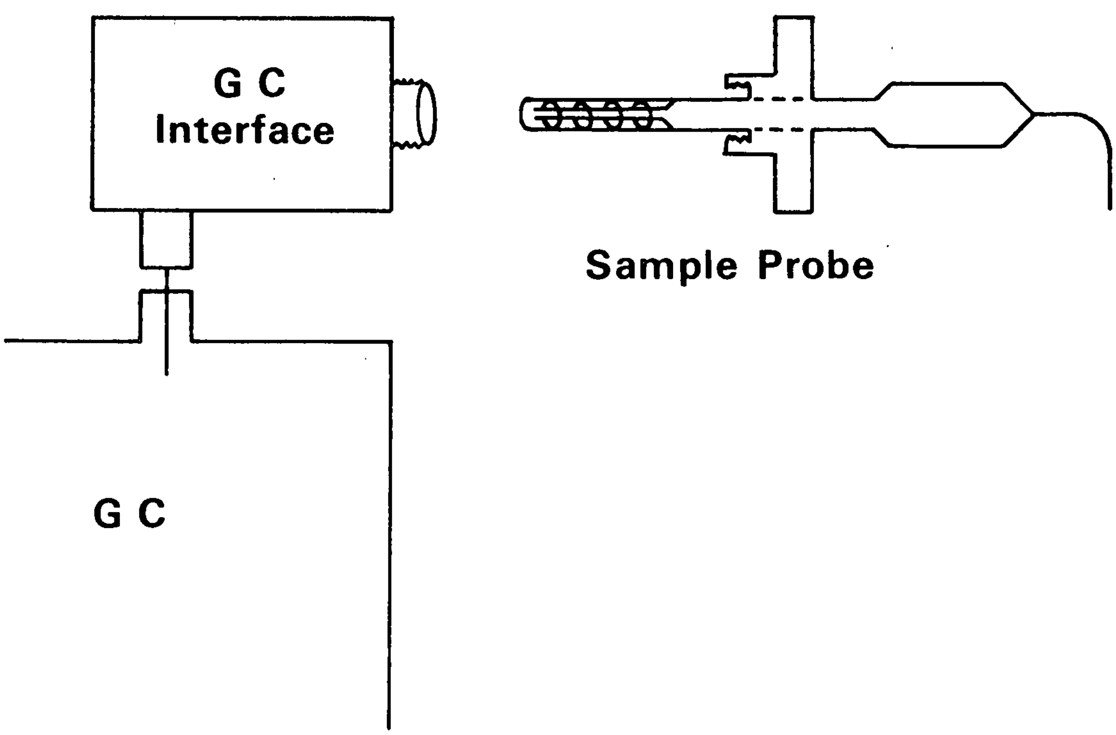
Pyrolysis Conditions

Prepyrolysis: 2 minutes at 400°C.

Pyrolysis: 10 seconds at 850°C.



Prepyrolysis assembly



Pyrolysis gas chromatography

GC Conditions

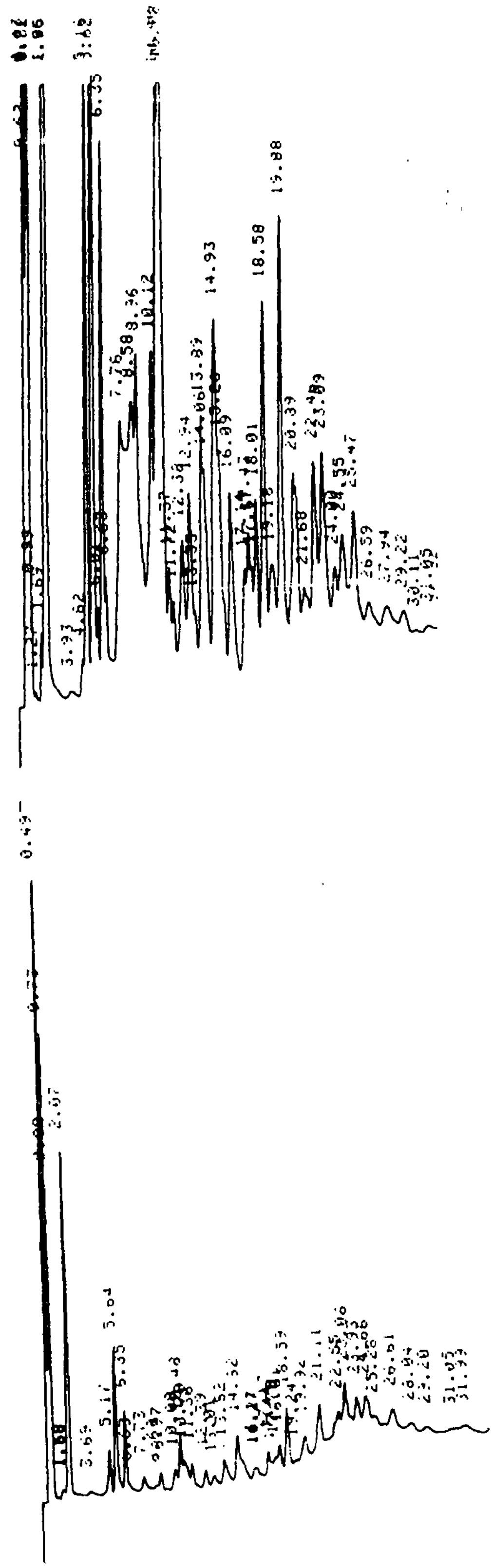
Packed glass column: 6 ft x 2 mm containing 1% SP 1000 on 60/80-mesh Carbopak B.

Column temperature: 40 to 200°C at 8°C/min

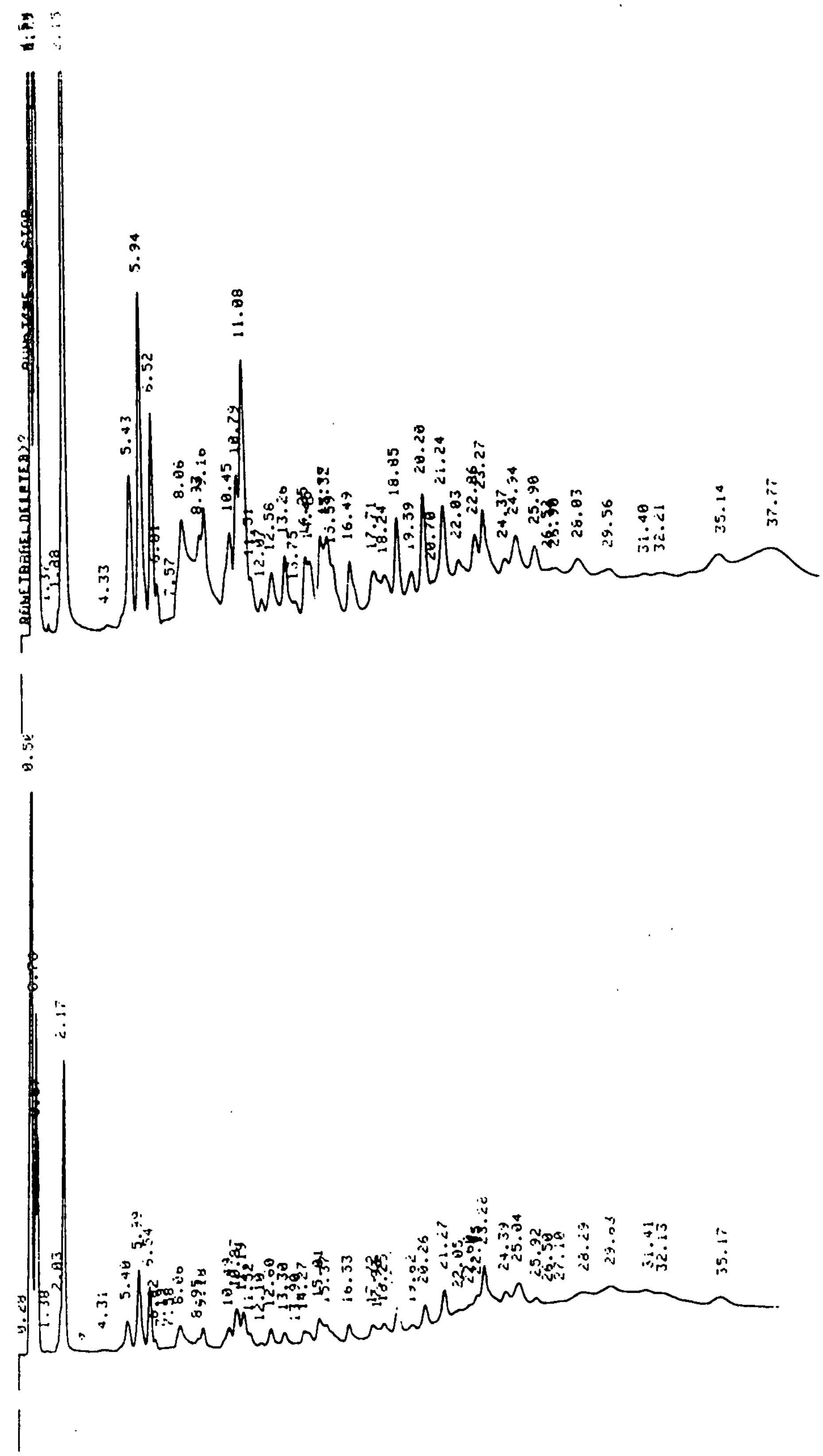
Detector (FID) 300°C. Injector 250°C.

Results and Discussion

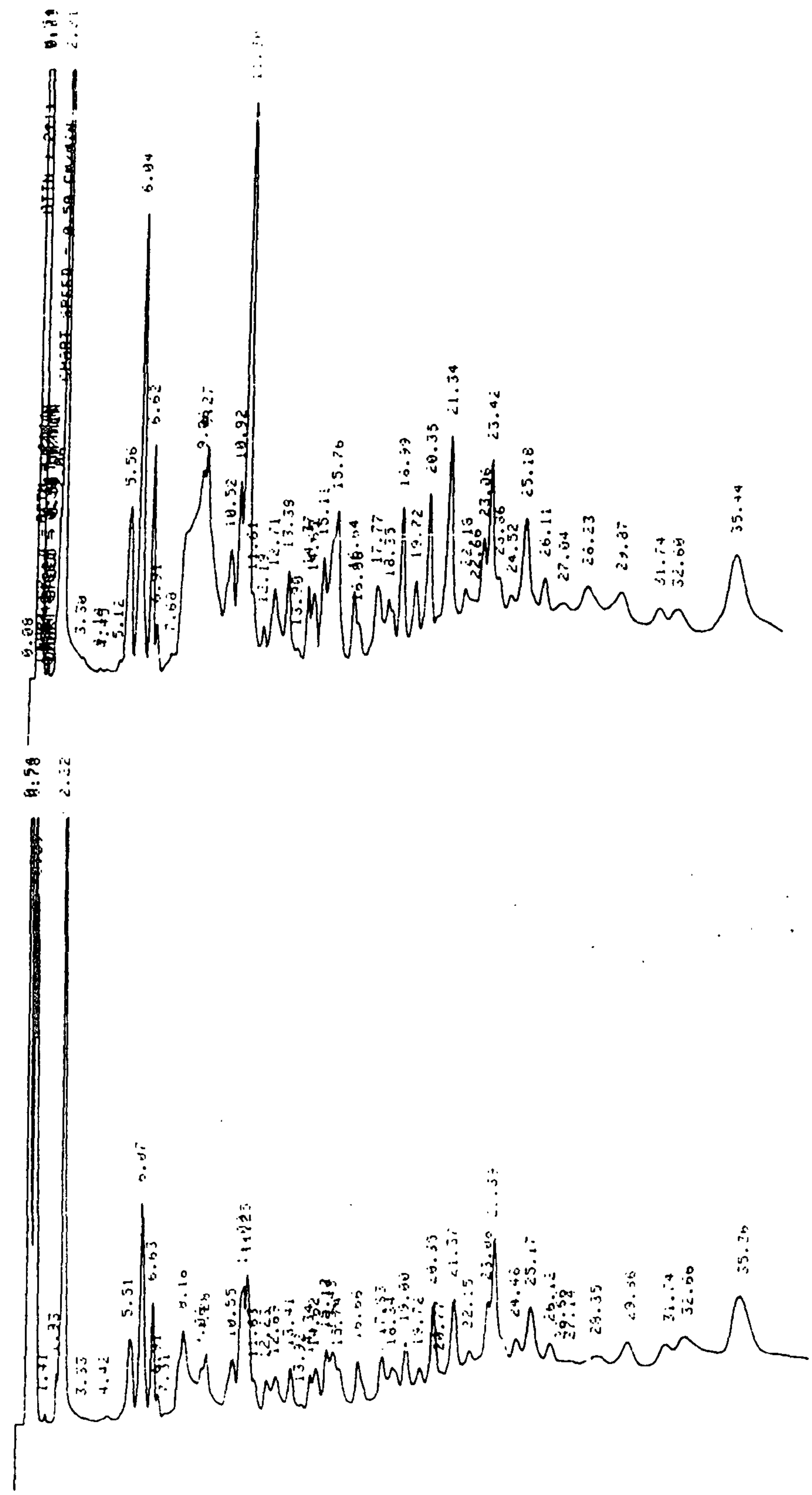
Removal of Paper Matrix with Prepyrolysis



Pyrogram of BL HW kraft and same after prepyrolysis



Pyrogram of UNBL SW kraft and same after prepyrolysis



Pyrogram of HW TMP fibers and same after prepyrolysis

Degree of Elimination of Different Fibers
with Prepyrolysis

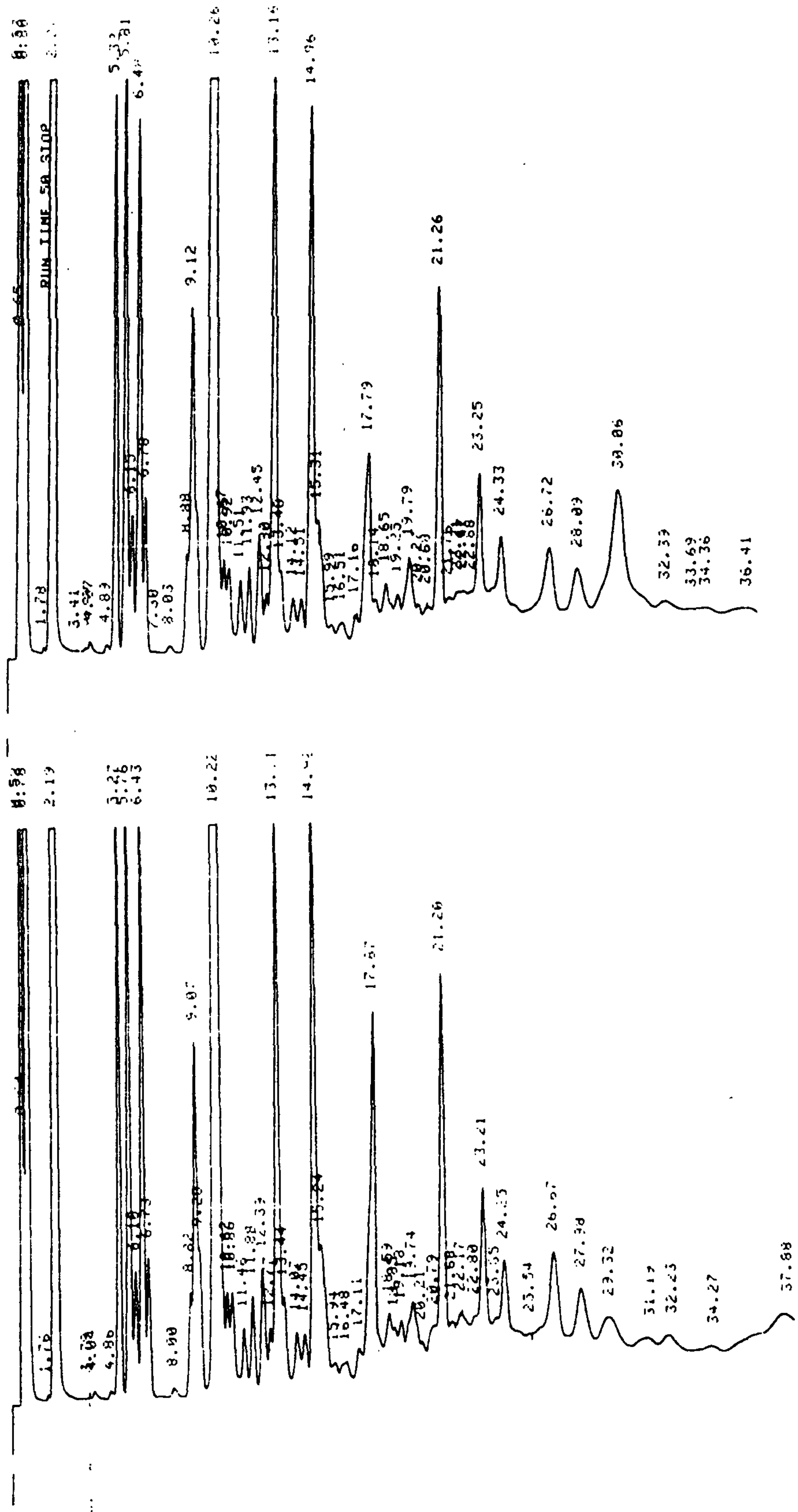
Sample	Retention Time of Major Peak, min.	Reduction of Peak Area, %
BL HW Kraft	10.73	96.9
UNBL SW Kraft	11.08	90.9
HW TMP	11.30	80.0

Effect of Prepyrolysis on Polymers

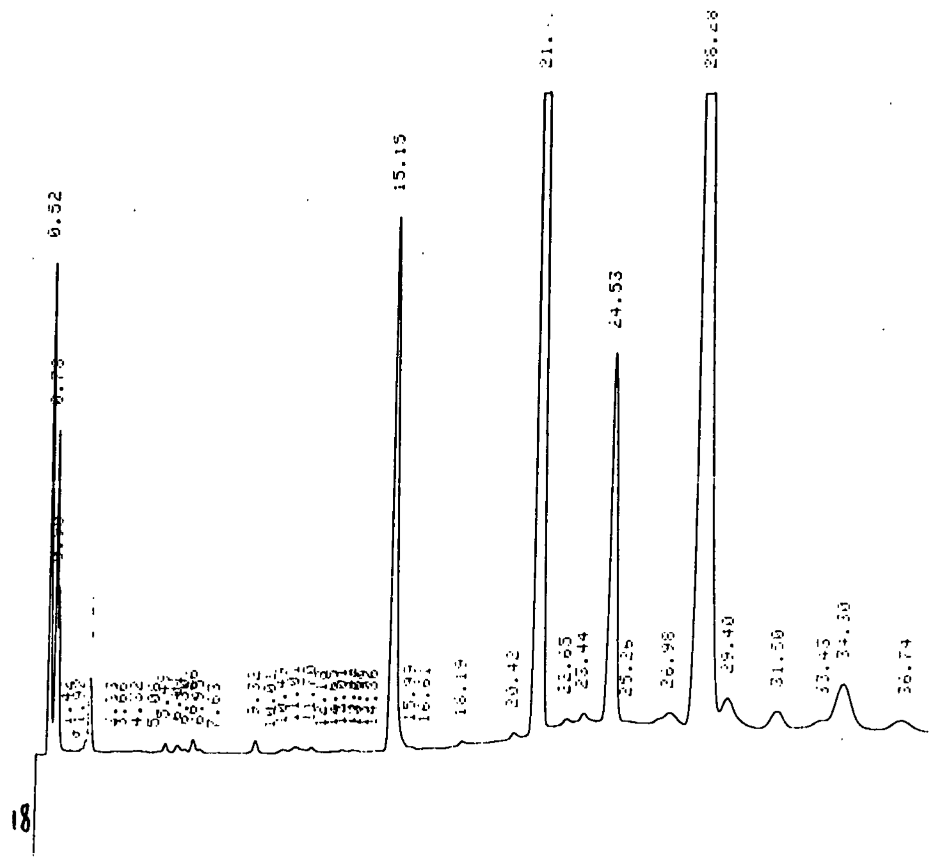
Sample	Retention Time of Major Peak, min.	Reduction of Peak Area, %
SBR	27.84	3.9
Polybutyl acrylate	13.09	12.6
Polyethyl acrylate	17.08	53.4
Polyethylene	15.54	50.2
Polypropylene	10.10	28.9
Polyvinyl butyral	10.26	14.8
Styrene maleic anhydride	27.84	51.2
Polyamide resin	15.53	4.3
ASB	28.22	12.9
Styrene isoprene	27.99	24.8
Ethylene vinyl acetate	6.46	3.3
Polystyrene	27.83	9.7

Effect of Prepyrolysis on Polymers

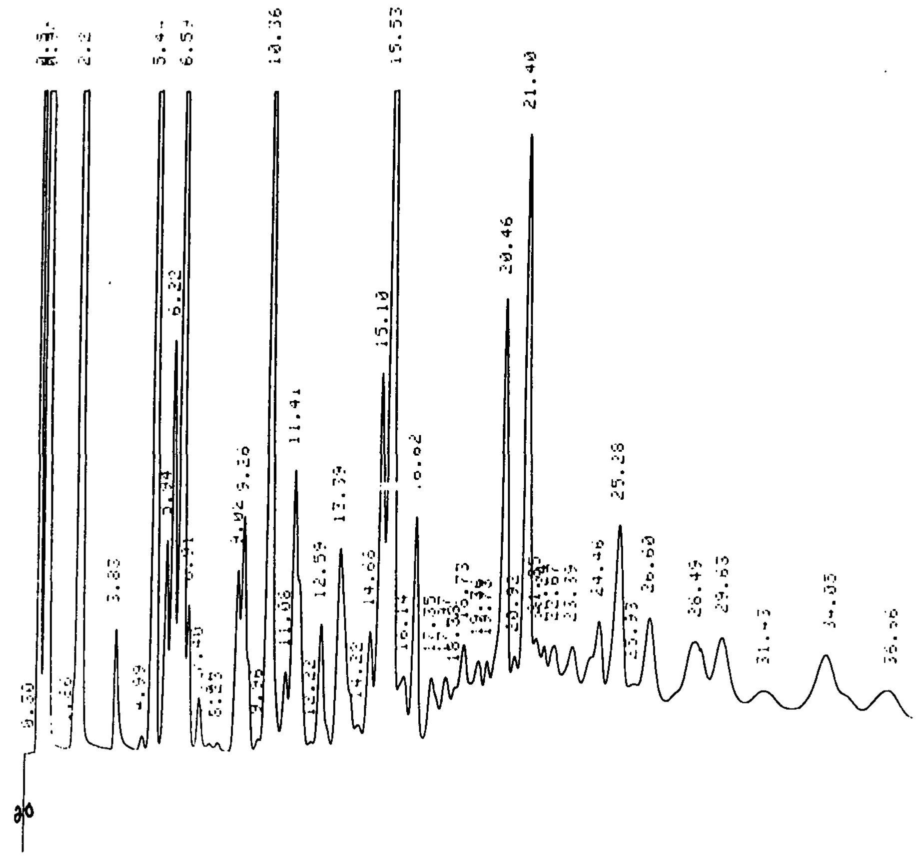
Sample	Retention Time of Major Peak, min.	Reduction of Peak Area, %
Polyvinyl alcohol	13.18	95.9
Melamine formaldehyde resin	No characteristic pattern	----
Polyvinyl acetate	12.27	90.4
Polyvinyl chloride	14.97	88.1
Polyvinylidene chloride	Very low response	----
Methyl cellulose	9.22	68.5
Cationic starch	5.95	77.9
Ethyl cellulose	4.23	60.7
Polyacrylamide	6.58	71.6



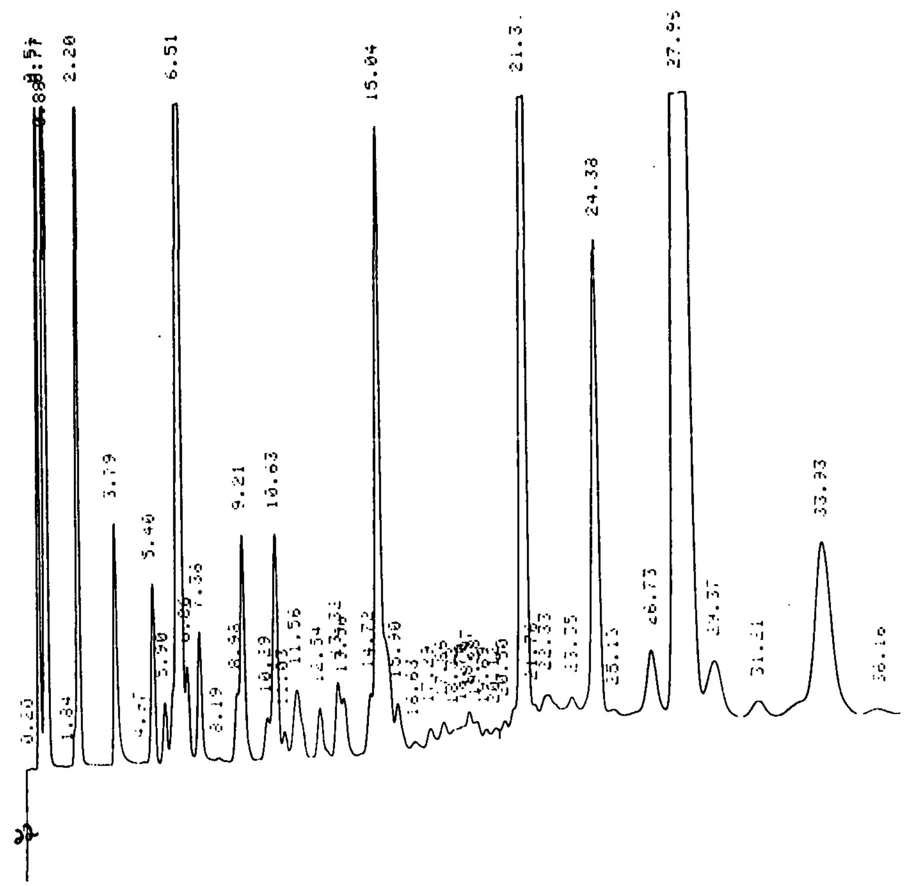
Pyrogram of polyvinyl butyral and same after prepyrolysis



Pyrogram of styrene maleic anhydride after prepyrolysis



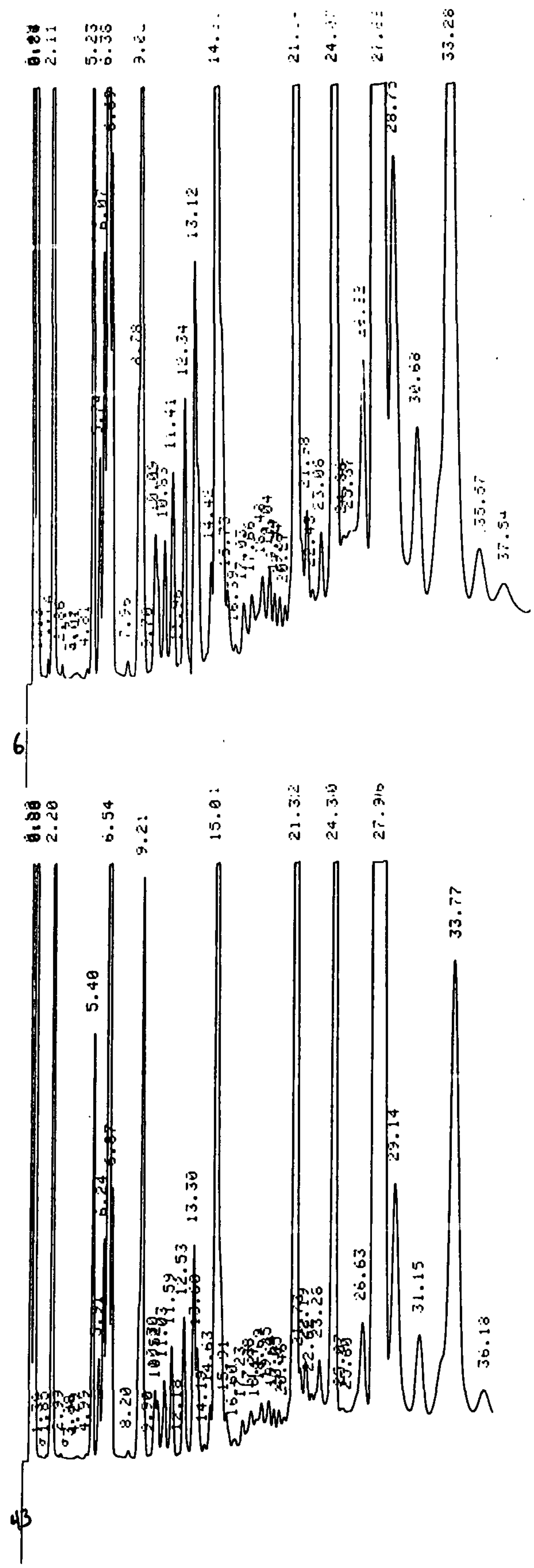
Pyrogram of polyamide resin after prepyrolysis



Pyrogram of ASB after prepyrolysis

Identification of Principal Peaks in Pyrogram
of Acrylonitrile Styrene Butadiene

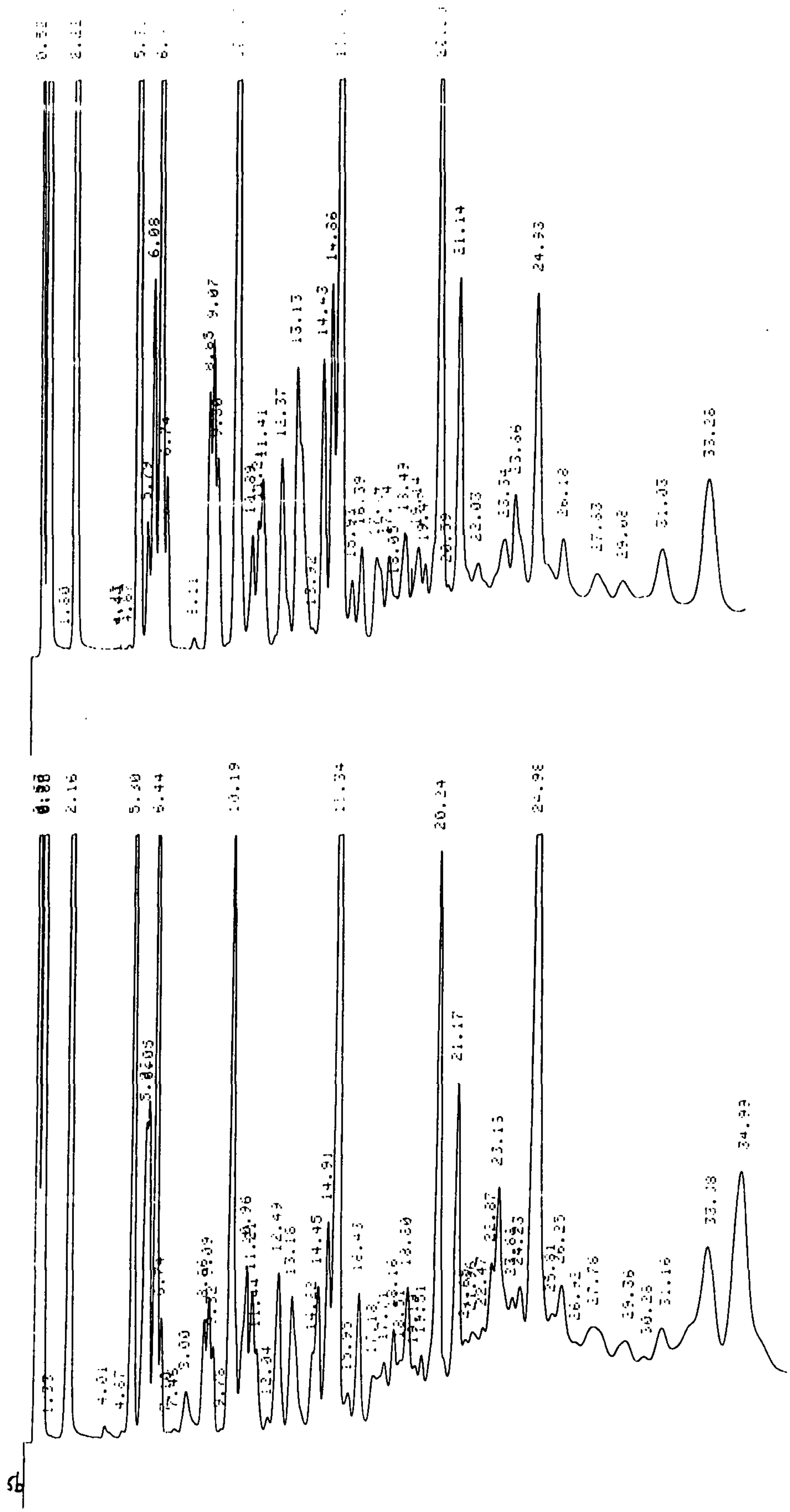
Retention Time, min	Compound
6.66	1,3-butadiene
15.15	benzene
21.43	toluene
24.52	ethylbenzene
28.22	styrene



Pyrogram of SBR alone (upper figure) and after addition to paper (lower figure), both after prepyrolysis.

Quantitative Determination of ASB in Paper

Run	Styrene Peak Area	Polymer Added, mg	Polymer Measured by PGC, mg
1	3531	0.15	0.19
2	3900	0.24	0.22



Pyrogram of polyethylene from library (upper figure) and in commercially prepared freezer wrap paper (lower figure), both after prepyrolysis.

Conclusions

1. Prepyrolysis can be used to destroy the paper matrix and simplify the identification of many polymers in paper by PGC.

2. The proper selection of pyrolysis and GC conditions can be used to develop a library of characteristic, fingerprint pyrograms useful for identification of polymers in paper.

3. The principal peaks in the pyrograms can be identified by mass spectrometry. This should enhance the power of PGC to identify polymers, especially in cases where characteristic fingerprint pyrograms are not obtained.

4. PGC can be used for semiquantitative analysis.

Future Work

Emphasize PGC/MS

Work with smaller amounts of polymer

Expand library of pyrograms with peaks identified by MS

Develop search routine to match identified peaks from unknown with those in library

Apply procedure to more real unknowns

Analysis of Pulping and Bleaching Liquors by Ion Chromatography

Problems in Ion Chromatographic Analysis

Additional Studies on the Ion Chromatographic Analysis of Pulping Liquors

Potential Sources of Error in Ion Chromatographic Analysis of Pulping Liquors

Instability of Liquor Samples

Homogeneity of Liquor and Representative Nature of Sample Taken for Analysis

Dilution Technique

Instability of Samples Diluted for Analysis

Chromatography

Actions to Improve Accuracy of Ion Chromatographic Analyses

- Run spiked samples every day
- Inject carbonate standard after each carbonate sample
- Run sample duplicates in random order
- Run sulfoxy standards three times per day
- Quantitate via internal standard method

Future Work

Develop internal standard method

Study stability of liquor samples during storage

Document the accuracy and precision of
liquor analyses by ion chromatography

Projects 3288 and 3521

Project 2926-10

R. H. Atalla

PROJECT 3288

FINE STRUCTURE OF WOOD PULP FIBERS

PROJECT 3521

RAMAN MICROPROBE INVESTIGATION OF
MOLECULAR STRUCTURE AND ORGANIZATION IN
THE NATIVE STATE OF WOODY TISSUE

PROJECT 2926-10

ON-LINE LIGNIN SENSOR

3288 STRUCTURE OF WOOD PULP FIBERS

I. CELLULOSE - WATER INTERACTIONS DURING THE DRYING PROCESS.

II. EFFECTS OF CONFORMATIONAL DISTRIBUTION OF CELLULOSE ON SHEET MECHANICAL PROPERTIES.

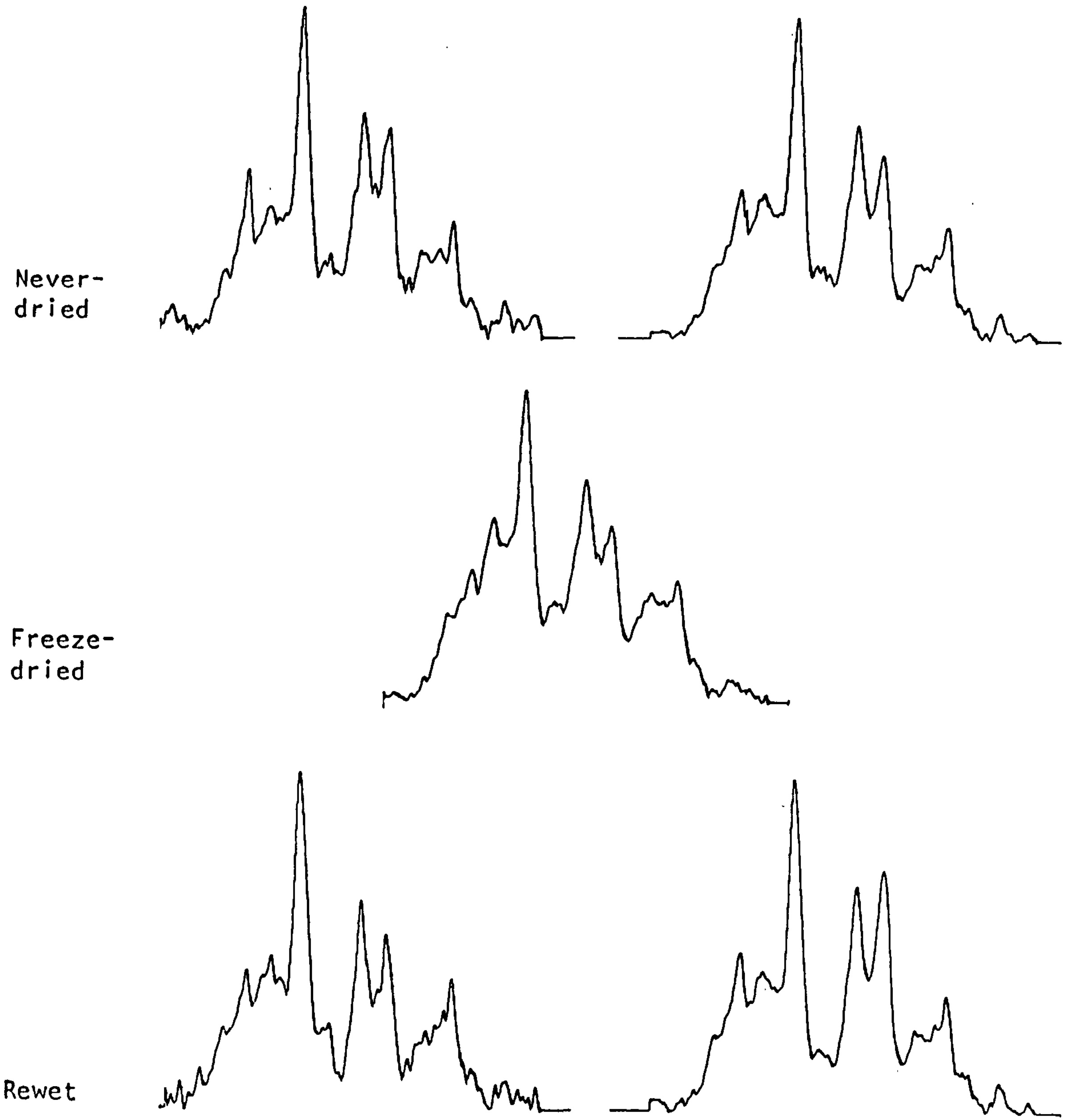
CELLULOSE - WATER INTERACTIONS

FINDINGS:

-- SIGNIFICANT QUALITATIVE DIFFERENCES ARE OBSERVED BETWEEN THE RAMAN SPECTRA OF WET AND DRIED PULPS.

-- THE DIFFERENCES INDICATE STRESS INDUCED LATTICE DISTORTIONS IN THE CELLULOSE WITHIN THE DRIED SAMPLES.

-- THE OBSERVED PHENOMENON IS REVERSIBLE TO VARYING DEGREES IN DIFFERENT CELLULOSES.



Raman spectra of never-dried, freeze-dried, and rewet bleached spruce kraft pulp.

KEY CONCLUSIONS:

-- DRYING OF CELLULOSIC FIBERS RESULTS IN DEVELOPMENT OF INTERNAL STRESSES WITHIN THE FIBER OF A MAGNITUDE NOT HERETOFORE RECOGNIZED.

-- SUCH STRESSES COULD WELL RESULT IN INTERNAL TENSILE FAILURE OF THE FIBRILS SUBJECTED TO THE HIGHEST STRESS; CYCLIC REPETITION OF THE WETTING AND DRYING PROCESS COULD RESULT IN PROGRESSIVE FAILURE OF THE INTERNAL LOAD-BEARING COMPONENTS OF INDIVIDUAL FIBERS.

FUTURE WORK:

-- MONITOR THE EFFECT OF MULTIPLE DRYING/REWETTING CYCLES.

-- CARRY OUT REWETTING STUDIES WITH DEUTERIUM OXIDE TO ASSESS THE DEGREE TO WHICH AGGREGATION DURING DRYING CAN BE IRREVERSIBLE.

EFFECTS OF CONFORMATIONAL DISTRIBUTION OF CELLULOSE ON SHEET MECHANICAL PROPERTIES

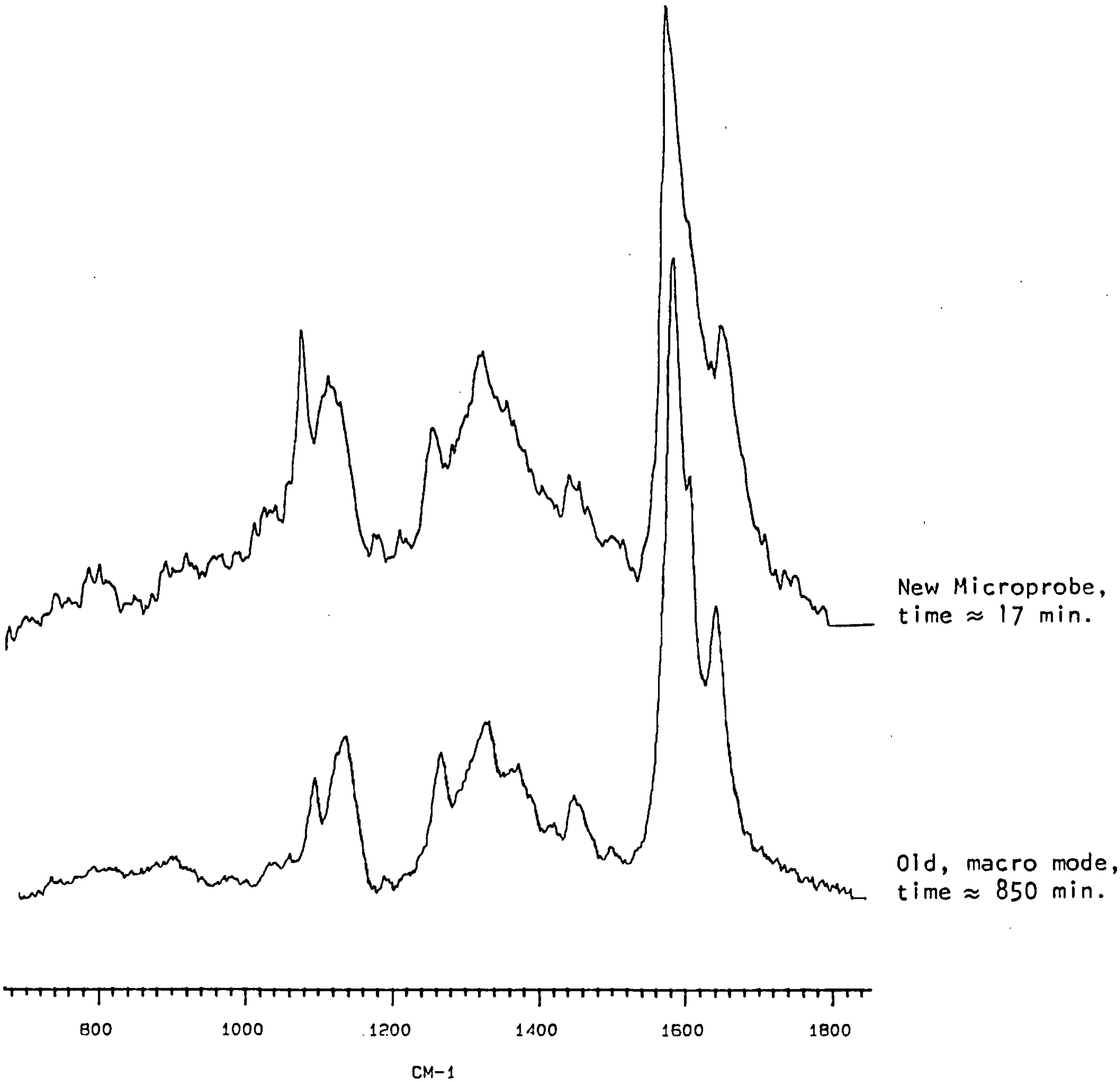
WE HAVE CARRIED OUT PRELIMINARY EXPERIMENTS TO INVESTIGATE THE CORRELATION BETWEEN CONFORMATIONAL DISTRIBUTION (K_I TO K_O RATIO) AND SHEET MECHANICAL PROPERTIES. THE RESULTS INDICATE THE EXISTENCE OF TRENDS IN THESE CORRELATIONS. THE EXPERIMENTS WERE MORE COMPLEX THAN WE ANTICIPATED, HOWEVER, AND WE PROPOSE TO REPEAT THEM AND PRESENT A REPORT ON THE RESULTS AT THE FALL MEETING.

PROJECT 3521 RAMAN MICROPROBE INVESTIGATION OF MOLECULAR STRUCTURE AND ORGANIZATION IN THE NATIVE STATE OF WOODY TISSUE

THE NEW RAMAN MICROPROBE SYSTEM HAS BEEN INSTALLED AND IS OPERATIONAL, ALTHOUGH A NUMBER OF ADDITIONAL ENHANCEMENTS ARE PLANNED.

KEY FEATURE:

-- GREATLY ENHANCED ON-CHANNEL INTEGRATION TIMES PROVIDE A HIGHER SIGNAL-TO-NOISE RATIO AND HIGHER RESOLUTION WITH A SUBSTANTIALLY REDUCED ACQUISITION TIME.



Comparison between old and new Raman systems of spectral quality and acquisition time associated with water-immersed Southern Pine groundwood.

OTHER FEATURES:

-- HIGH QUALITY ZEISS MICROSCOPE WITH SUPERIOR IMAGING CAPABILITIES

-- MULTI-TASKING, ALLOWING SIMULTANEOUS DATA ACQUISITION AND WORKUP OR OUTPUT

-- RAPID PLOTTING; IBM COMPATIBLE DATA; HIGH SPEED; LARGE MEMORY; USER FRIENDLY

THE NEW RAMAN MACRO SYSTEM IS STILL BEING OPTIMIZED, WITH THE NEEDS OF THE ON-LINE DETECTION CAPABILITY THE PRIMARY TARGET.

-- THE NEW YAG/DYE LASER SYSTEM IS OPERATIONAL.

-- THE GATABLE DETECTOR HAS BEEN RETURNED TO THE MANUFACTURER BECAUSE OF DEFECTIVE DIODES IN THE ARRAY; WE EXPECT TO HAVE IT RETURNED WITHIN THE NEXT FEW WEEKS.

-- WE ARE WORKING ON OPTIMIZING THE MATCH BETWEEN THE REPETITION FREQUENCY OF THE LASER AND THE OPTIMUM GATING FREQUENCY OF THE DETECTOR.

OPPORTUNITIES ARISING FROM THE NEW RAMAN MICROPROBE SYSTEM

A. MAPPING OF BOTH ORIENTATIONAL AND COMPOSITIONAL VARIATIONS IN NATIVE WOODY TISSUE

B. MAPPING OF THE EFFECTS OF DELIGNIFICATION REACTIONS ON LIGNIN DISTRIBUTION ACROSS THE CELL WALLS

C. TIME RESOLVED STUDIES TO SEPARATE RAMAN SPECTRA FROM FLUORESCENCE, AND TO STUDY THE RISE AND DECAY OF ELECTRONIC EXCITATION

D. THE POSSIBILITY OF AN ON-LINE LIGNIN DETECTOR

ON-LINE LIGNIN SENSOR

(2926-10)

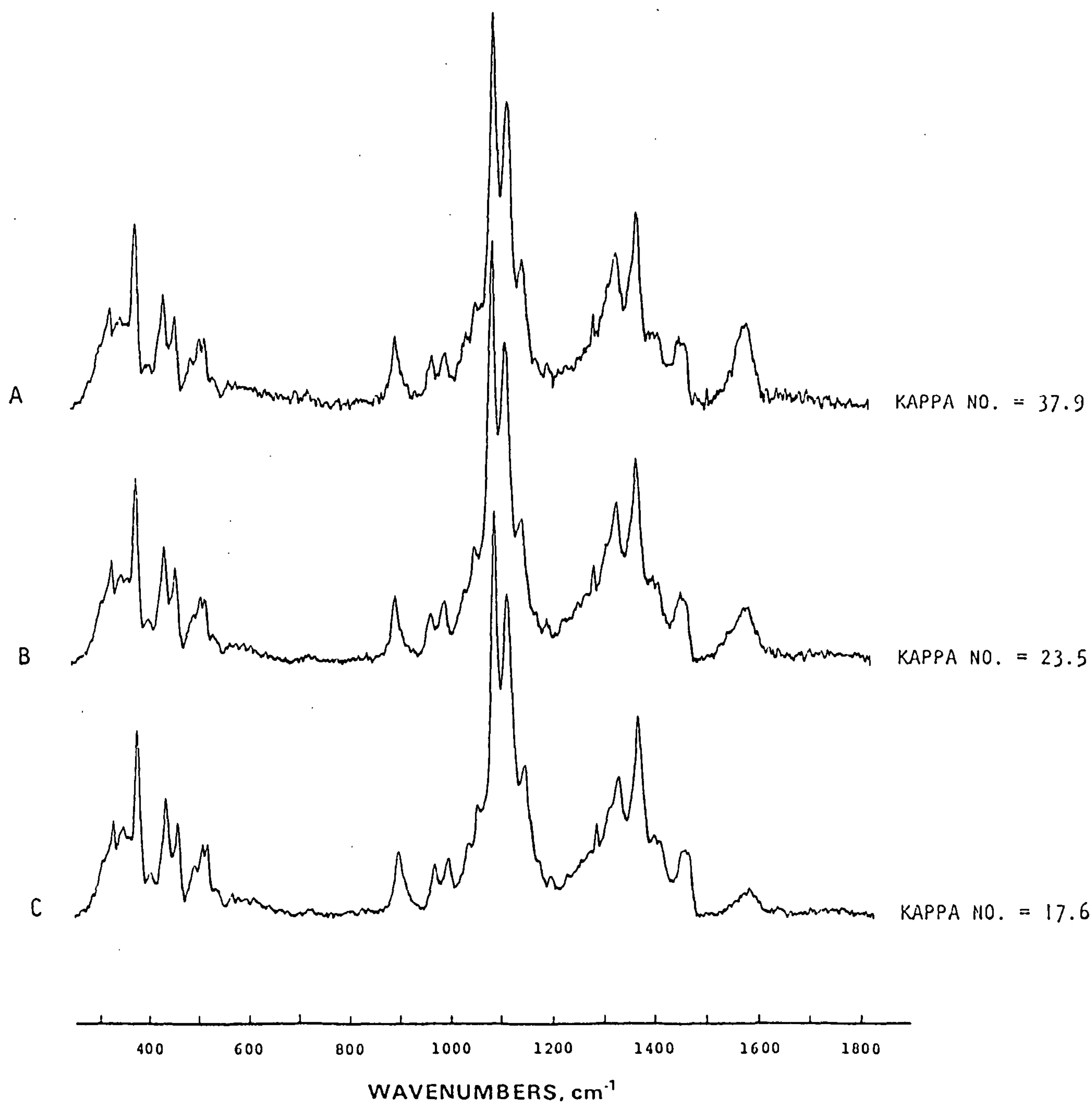
RESULTS TO DATE:

1. DEMONSTRATED THAT RAMAN SPECTRA CAN BE ACQUIRED FOR WATER IMMERSED SAMPLES OF HOLOPULP, ASPEN KRAFT, AND SULPHITE AQ PULPS.

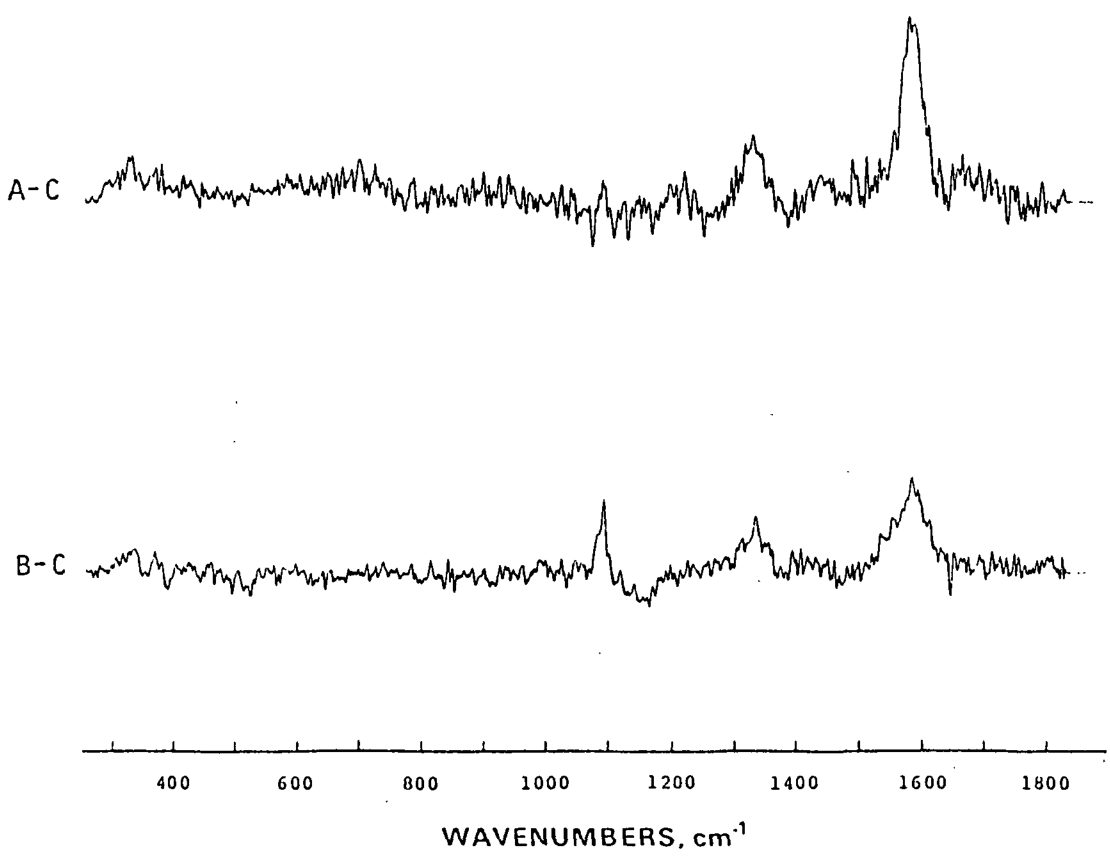
2. FOUND THAT VARIATION OF THE 1600 CM^{-1} BAND, CHARACTERISTIC OF THE AROMATIC RINGS IN LIGNIN, IS LINEAR WITH LIGNIN CONTENT FOR THE SOUTHERN PINE HOLOPULP.

3. FOUND THE RAMAN SPECTRA OF KRAFT PULPS CONTAIN INFORMATION OTHER THAN THE TOTAL LIGNIN CONTENT; THIS INFORMATION IS ALSO POTENTIALLY USEFUL FOR ON-LINE CONTROL PURPOSES.

RAMAN SPECTRA OF ASPEN KRAFT PULP



RAMAN DIFFERENCE SPECTRA (ASPEN KRAFT)



DIRECTIONS FOR FUTURE WORK:

1. CONTINUE ASSEMBLY OF THE PULSED LASER AND SPECTROMETER SYSTEM FOR RAPID ACQUISITION OF THE SPECTRA.

2. INTERPRETATION OF LIGNIN SPECTRAL FEATURES OTHER THAN THE 1600 CM^{-1} BAND.

Project 3474

Tom McDonough

PROJECT 3474

IMPROVED PROCESSES FOR BLEACHED CHEMICAL PULP

OBJECTIVE

DECREASE OR ELIMINATE THE NEED FOR CHLORINE-BASED DELIGNIFICATION

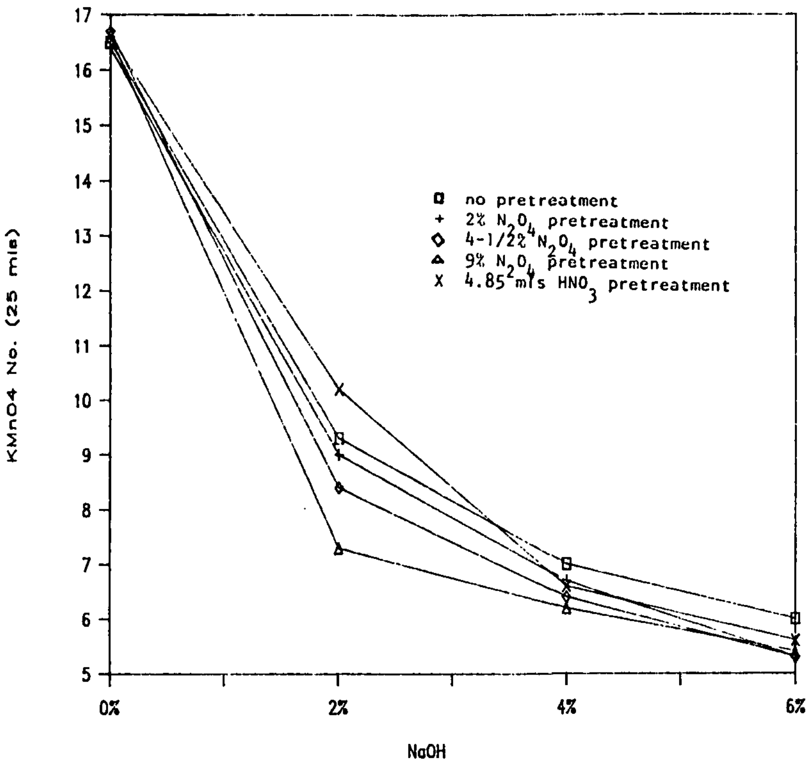
PROJECT 3474

RESEARCH AREAS

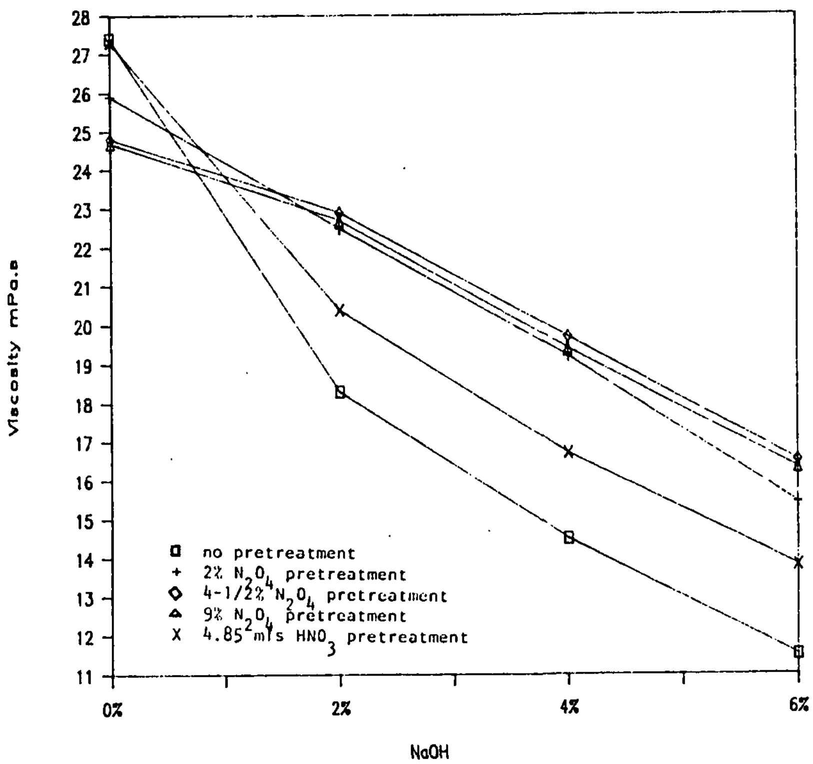
- EFFECTS AND MECHANISM OF NO_2 PRETREATMENT
- ALTERNATIVES TO NO_2
- PEROXIDE DELIGNIFICATION
- SULFITE-AQ KINETICS (STUDENT RESEARCH)
- CHLORINATION KINETICS (STUDENT RESEARCH)
  - LOW CONSISTENCY
  - MEDIUM CONSISTENCY

EFFECTS AND MECHANISM OF NO_2 PRETREATMENT

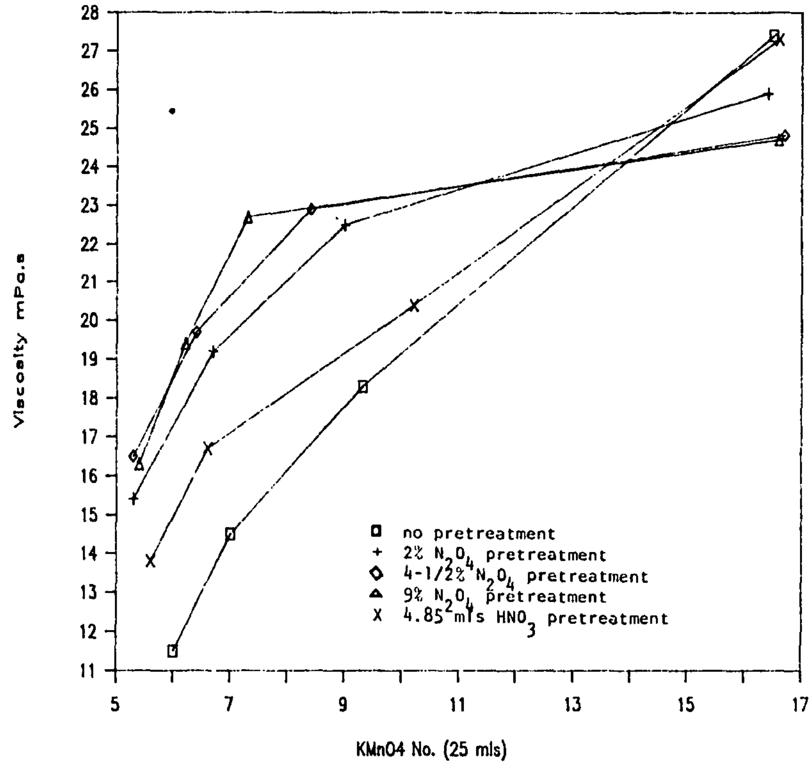
- CONFIRMATION AND CHARACTERIZATION OF EFFECTS
- EFFECTS IN HARDWOOD DELIGNIFICATION
- LOW NO_2 APPLICATIONS
- COMBINATIONS OF NO_2 AND OTHER REAGENTS
- FTIR STUDY OF HIGH KAPPA PULP



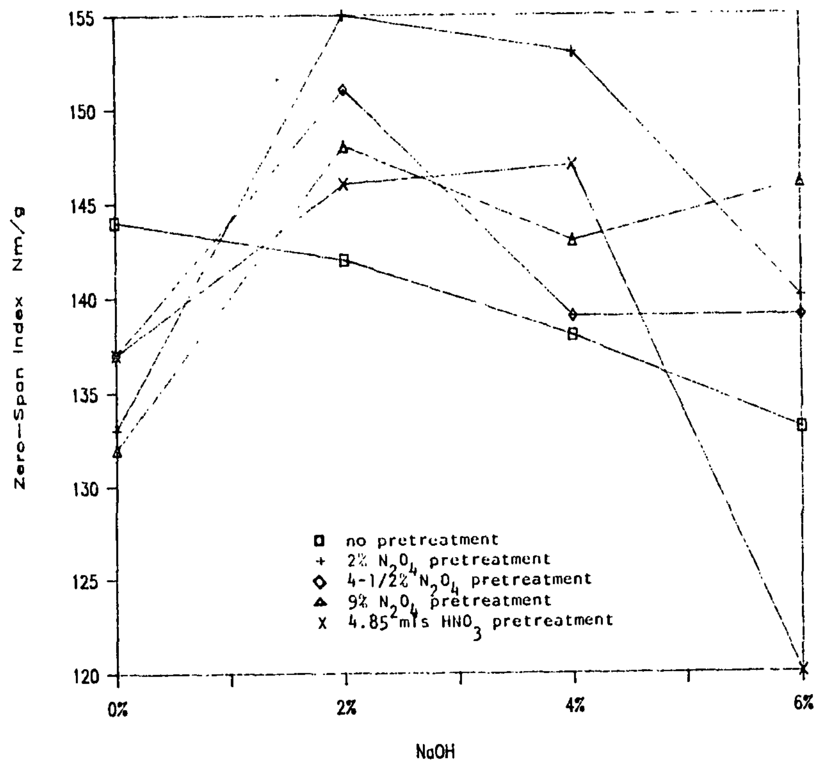
Effects of N_2O_4 pretreatment on K number after subsequent oxygen bleaching with varied charges of NaOH in the oxygen stage.



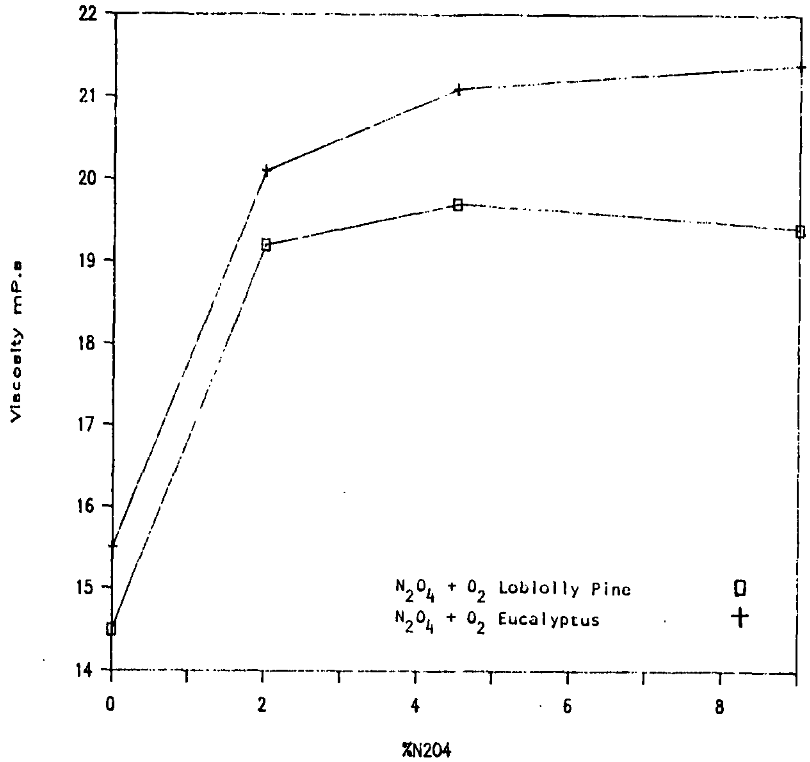
Effects of N_2O_4 pretreatment on K number after subsequent oxygen bleaching with varied charges of NaOH in the oxygen stage.



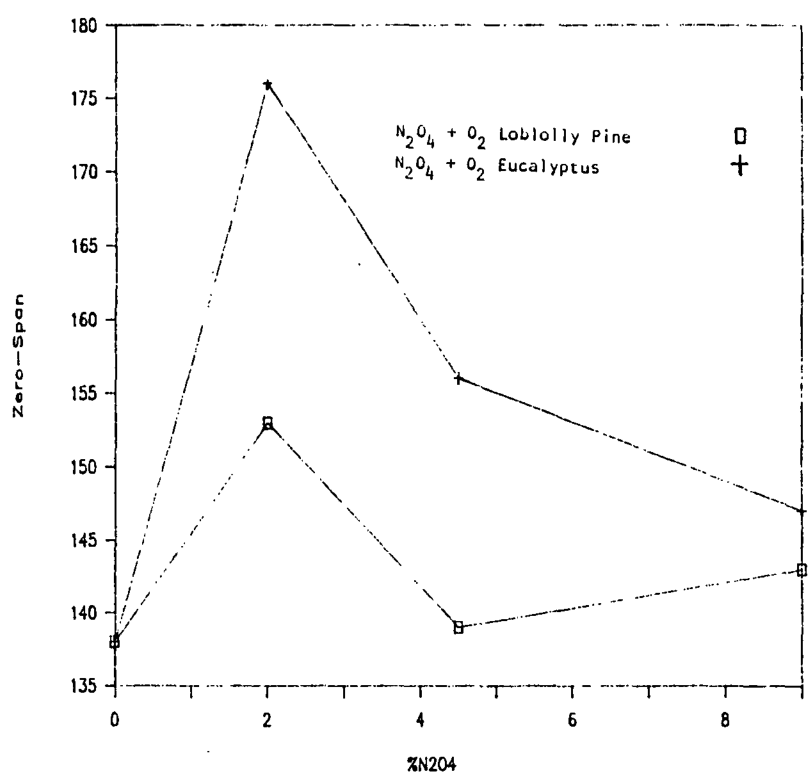
Effects of N_2O_4 pretreatment on selectivity of a subsequent oxygen stage.



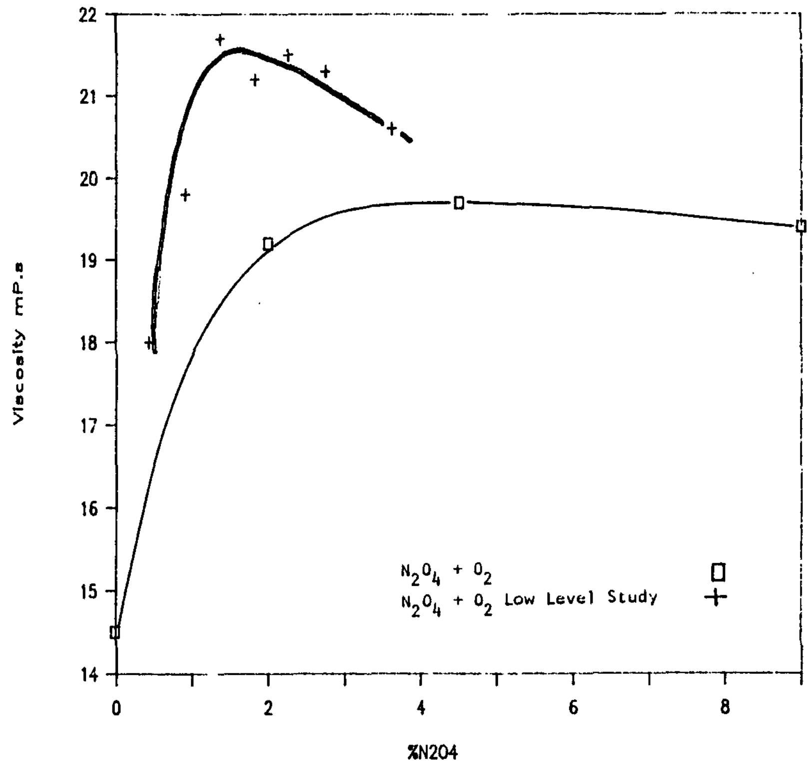
Effects of N_2O_4 pretreatment and subsequent oxygen bleaching on zero span tensile strength.



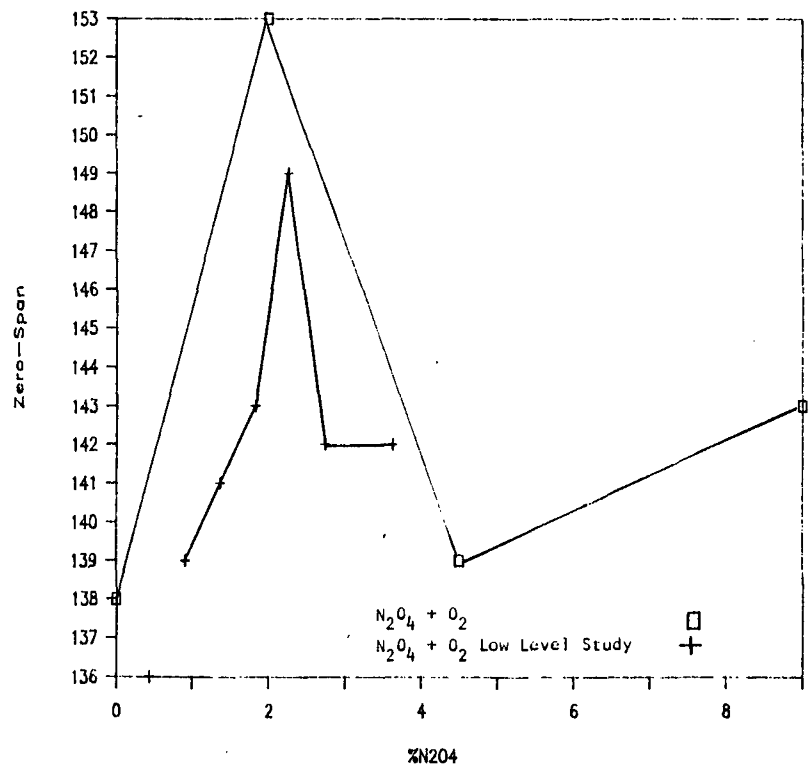
Effects of N_2O_4 treatment before oxygen bleaching with 4% NaOH on viscosity of pine and eucalyptus kraft pulps.



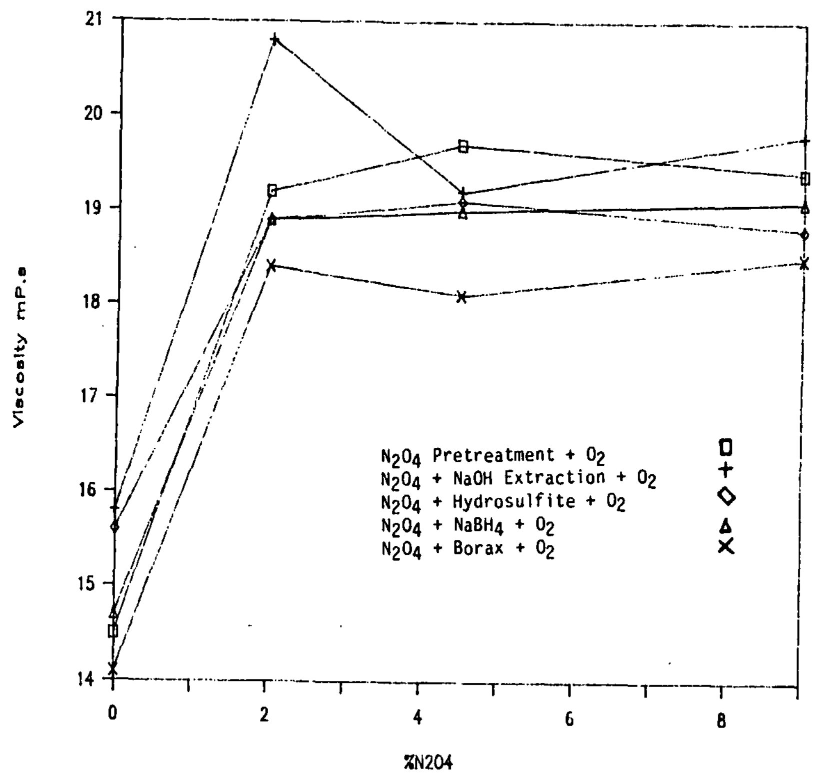
Effect of N_2O_4 treatment before oxygen bleaching with 4% NaOH on zero span tensile strength of pine and eucalyptus kraft pulps.



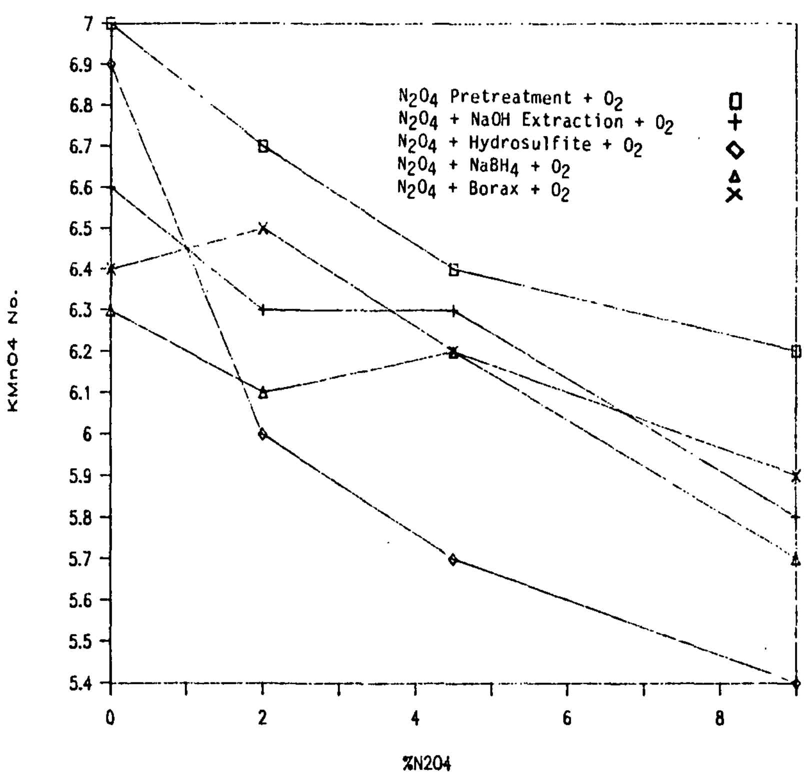
Effects of N_2O_4 treatment before oxygen bleaching with 4% NaOH on viscosity of pine pulps. The two series of experiments were done on different occasions.



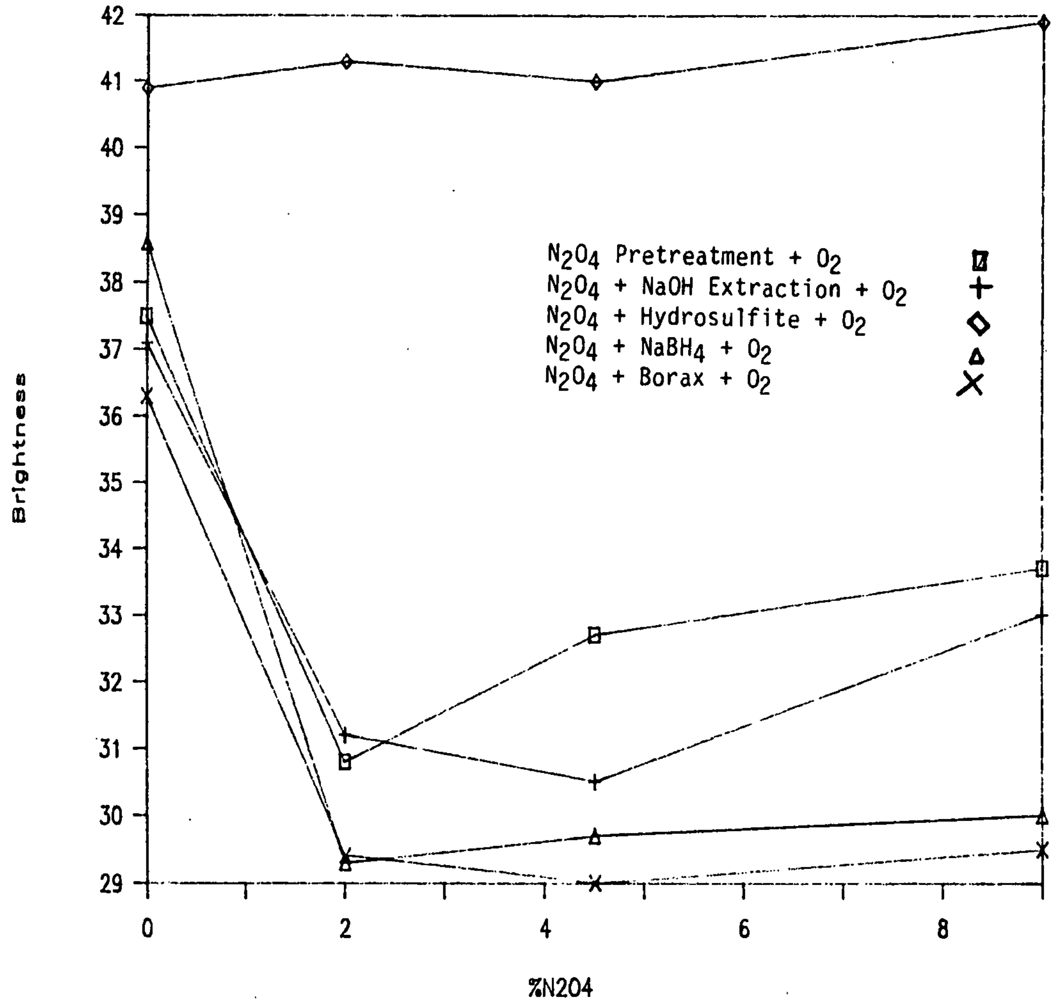
Effects of N_2O_4 treatment before oxygen bleaching with 4% NaOH on viscosity of pine pulps. The two series of experiments were done on different occasions.



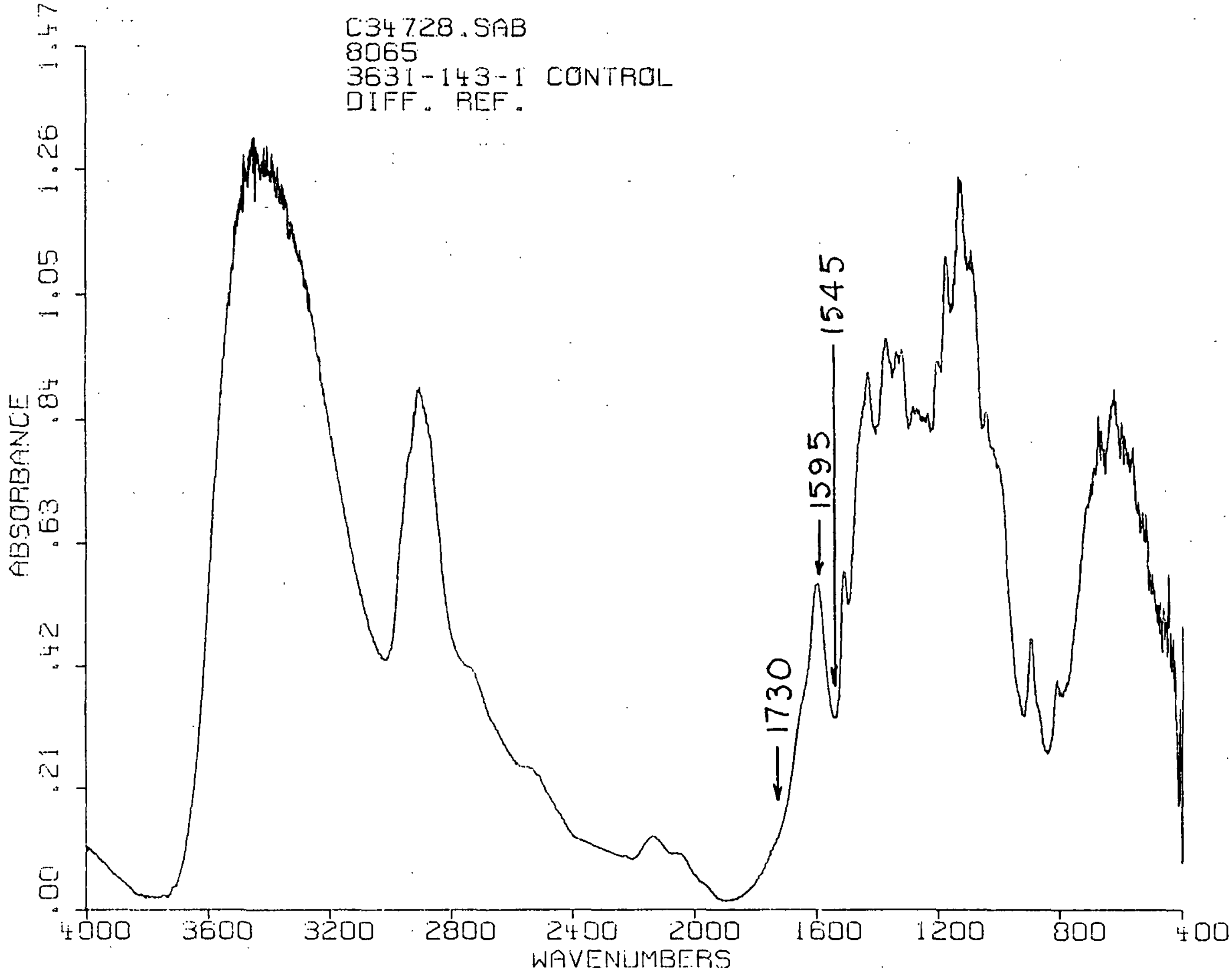
Effects of inserting additional treatments between N_2O_4 and oxygen (4% NaOH) on pulp viscosity.



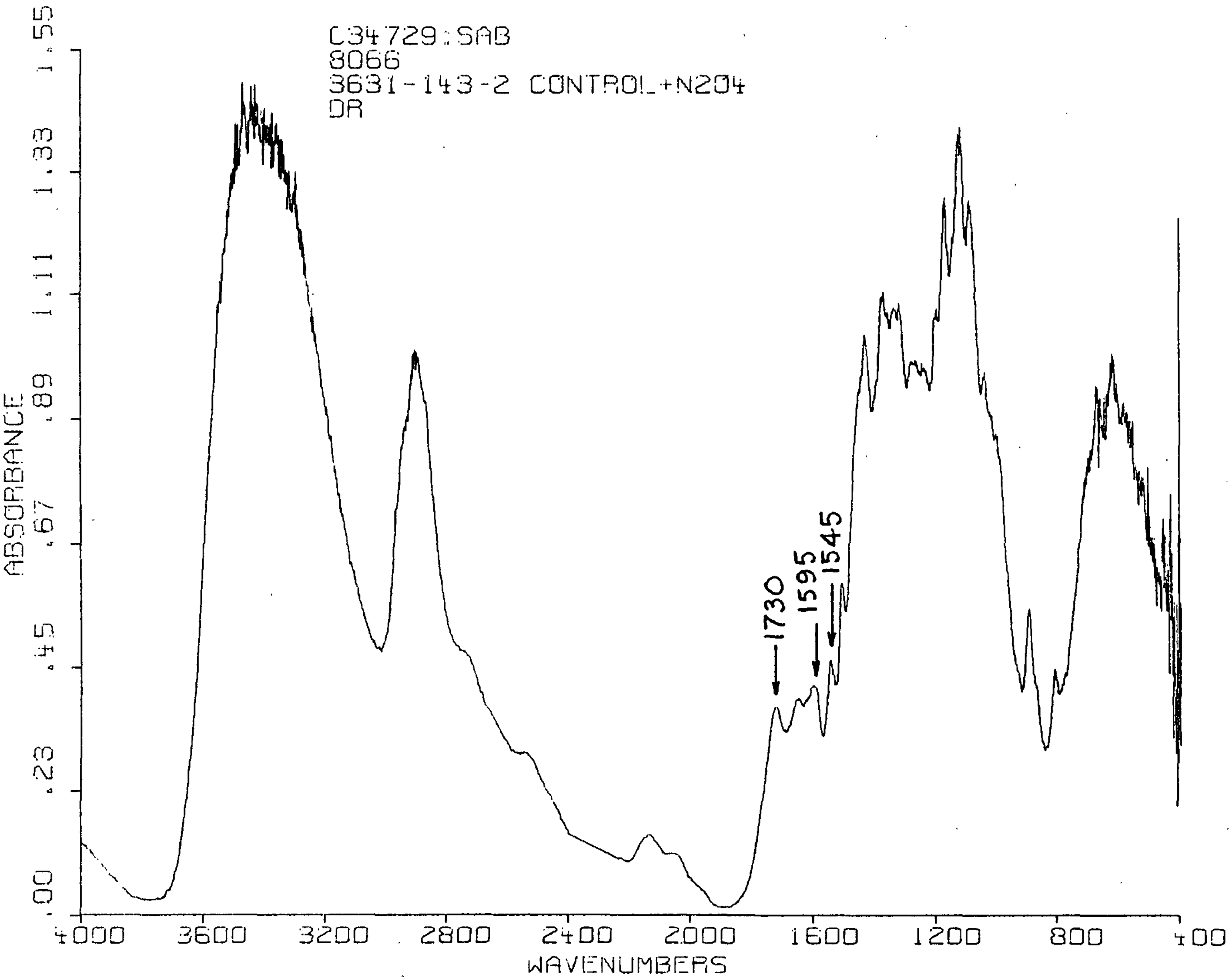
Effects of inserting additional treatments between N_2O_4 and oxygen (4% NaOH) on K number.



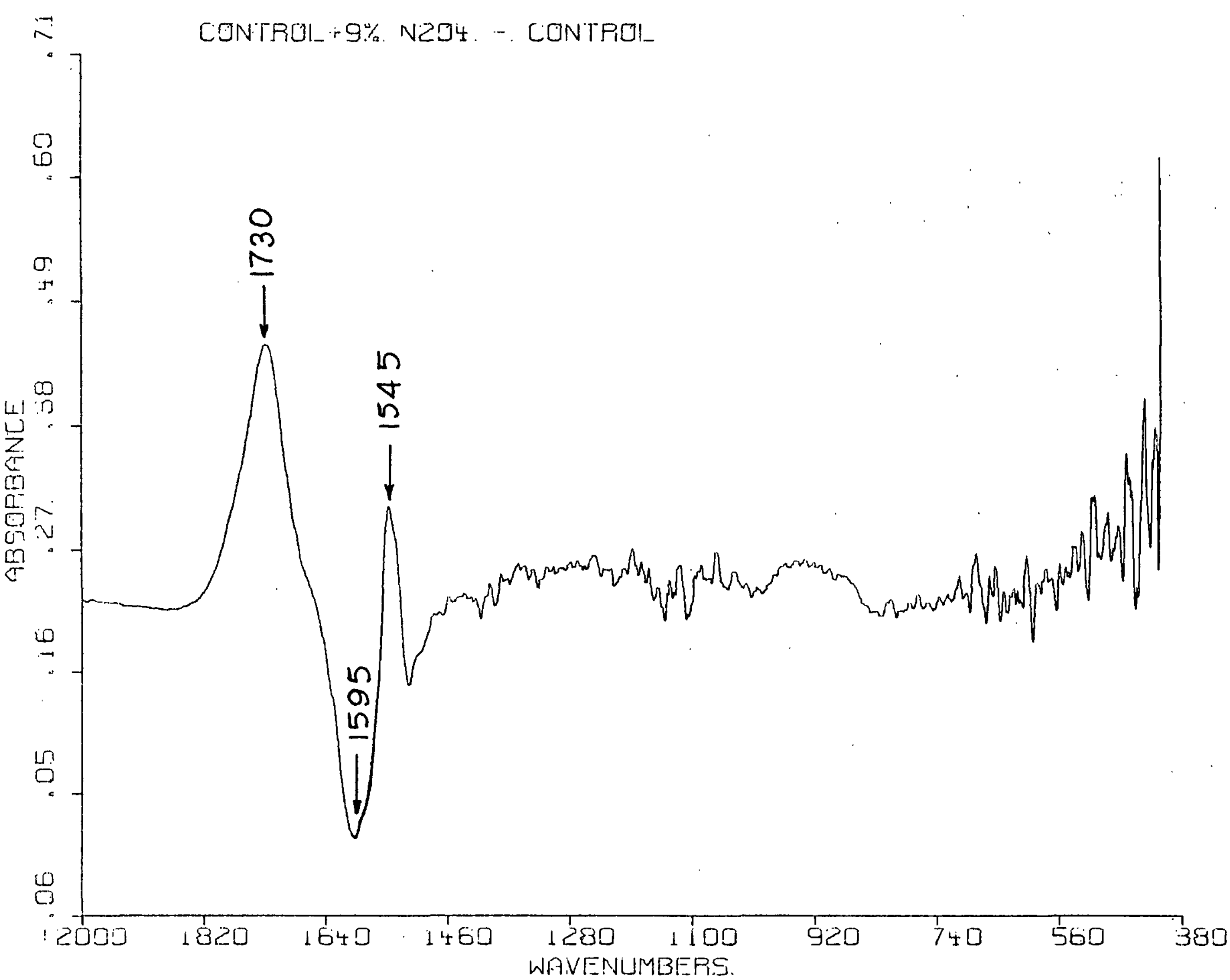
Effects of inserting additional treatments between N_2O_4 and oxygen (4% NaOH) on brightness.



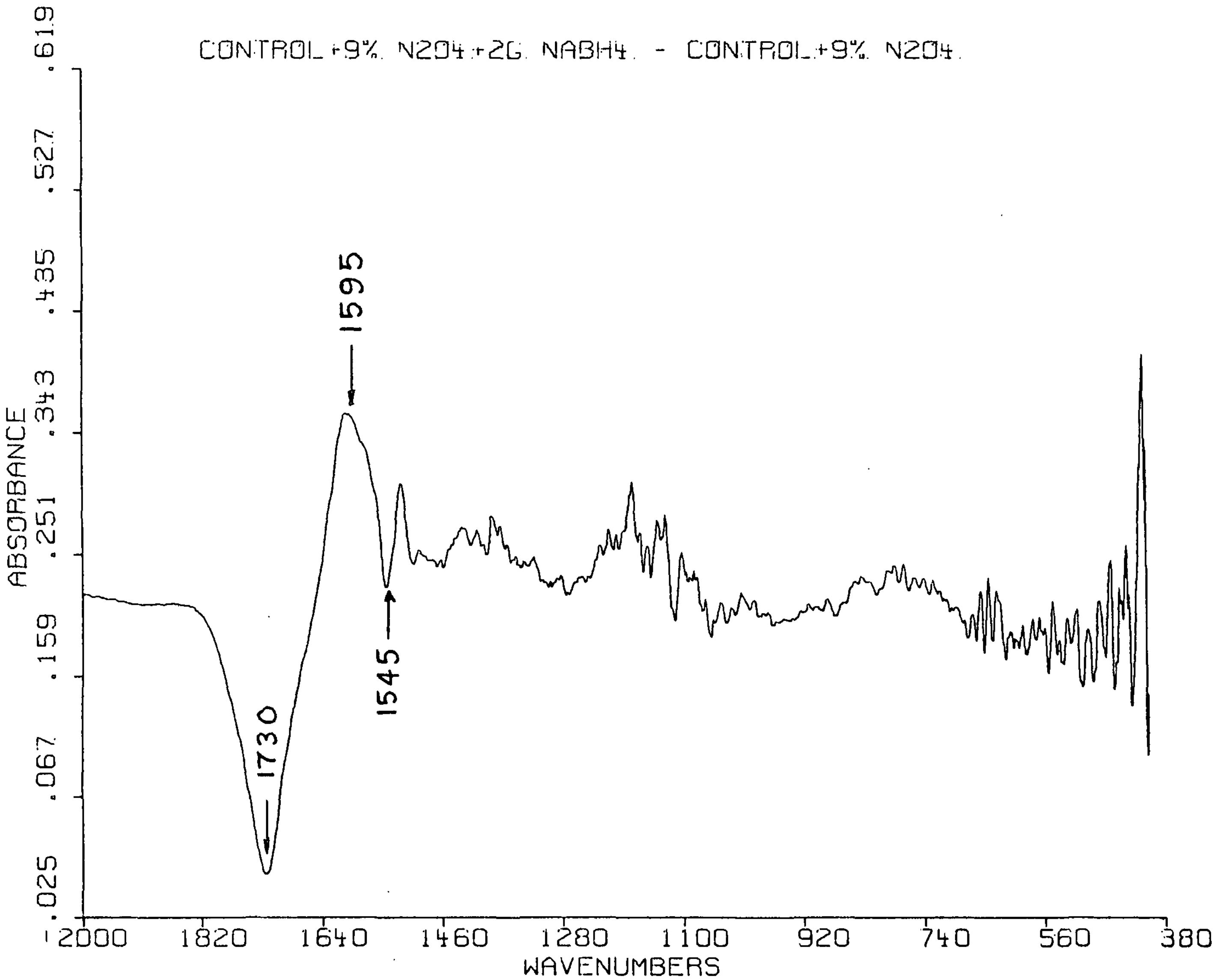
FTIR Spectrum of kraft pulp (control)



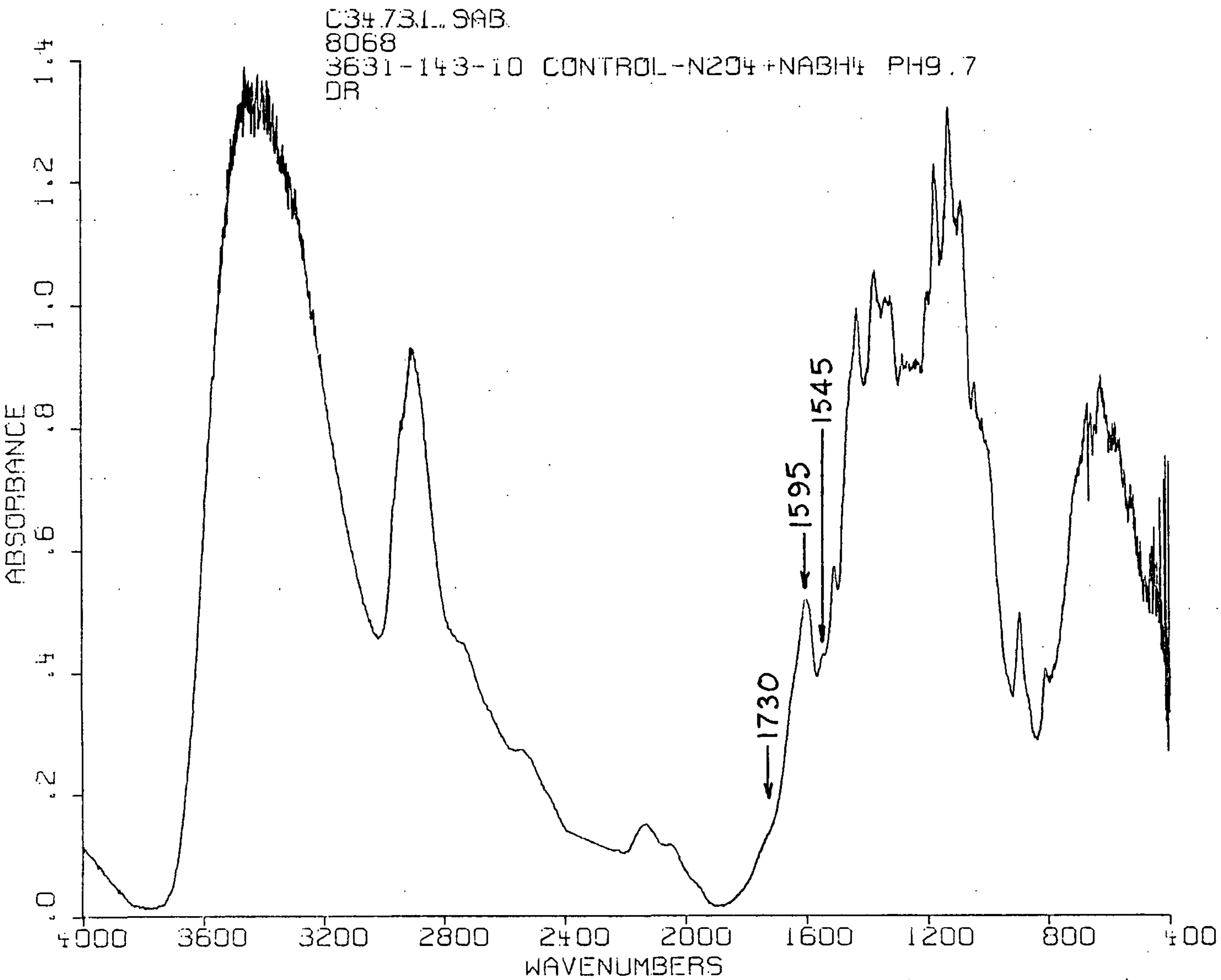
FTIR spectrum of N_2O_4-treated kraft pulp (control + N_2O_4).



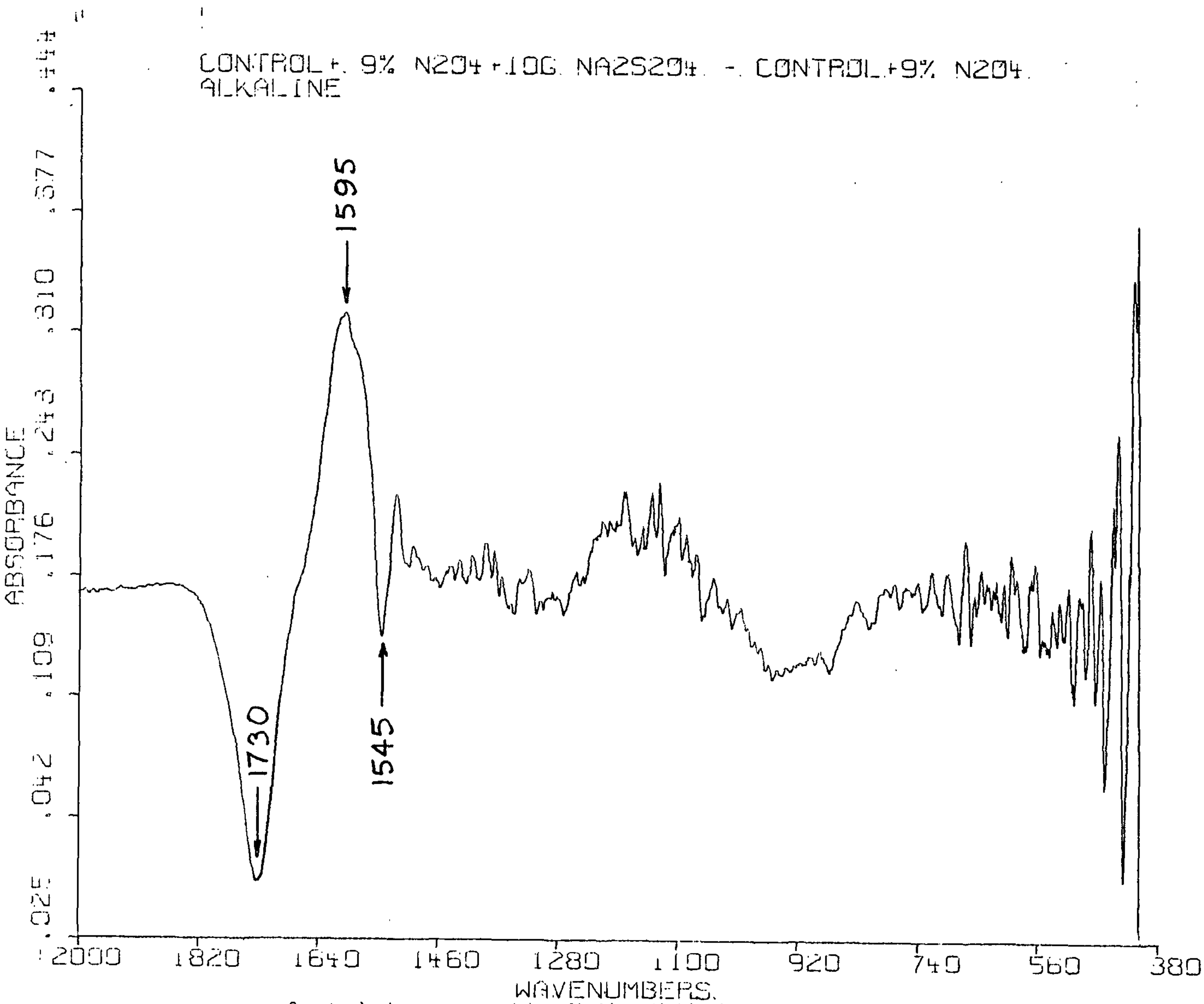
Spectral changes caused by N_2O_4 treatment.



Spectral changes caused by alkaline borohydride reduction of N_2O_4 treated pulp.



FTIR spectrum of N_2O_4-treated kraft pulp after further treatment with $NaBH_4$ (control + N_2O_4 + $NaBH_4$)



Spectral changes caused by alkaline dithionite reduction of N_2O_4 treated pulp.

△ Fe

□ Control

⇧ Mn

⬡ Cu

◇ FC

THE INSTITUTE OF PAPER CHEMISTRY

M E M O R A N D U M

FROM Institute Activities Association DATE March 25, 1987

TO Staff and Students

SUBJECT IPC Softball Teams

All men interested in playing slow pitch softball this summer should contact Walter Rantanen (Ext. 415). The team is in the Men's Industrial League and plays on Monday night.

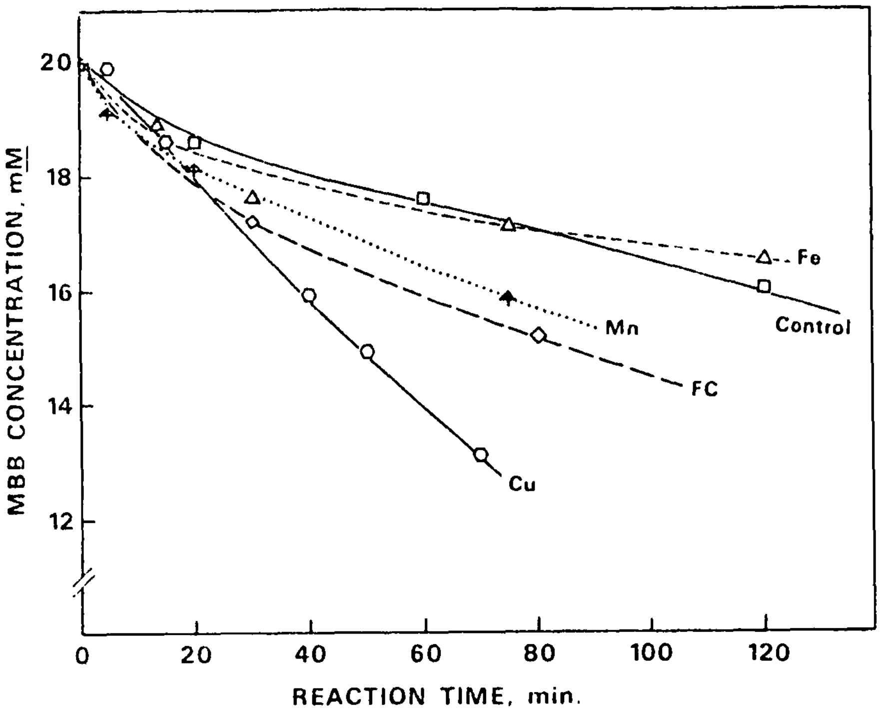
All women interested in playing slow pitch softball this summer should contact Barbara Burns (Ext. 246). The team is playing on Monday night.

ALTERNATIVES TO NO_2

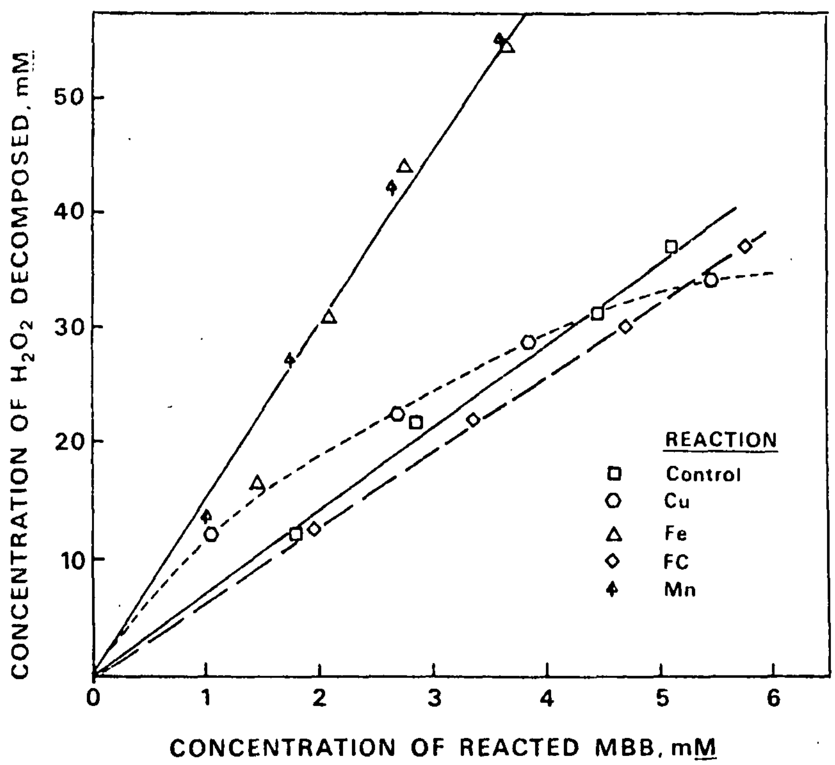
- BR_2
- $NO_2 + BR_2$
- CH_3CO_3H
- OTHER ELECTROPHILES
- OTHERS SUGGESTED BY STUDIES OF NO_2 MECHANISMS

PEROXIDE DELIGNIFICATION

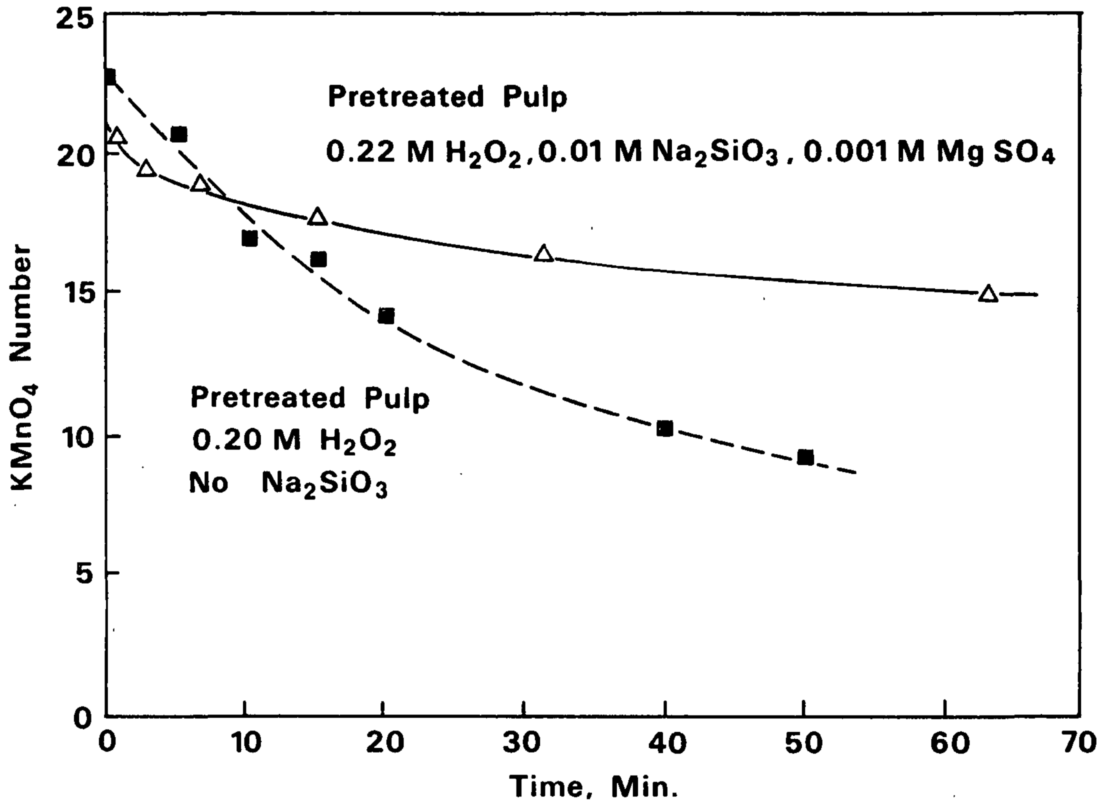
- STUDENT RESEARCH
  - CATALYSIS IN MODEL COMPOUND OXIDATION
  - RELATIONSHIP OF DELIGNIFICATION TO DECOMPOSITION
  - SELECTIVITY IMPROVEMENT
- FOLLOW-UP TO STUDENT RESEARCH
  - CATALYST EVALUATION



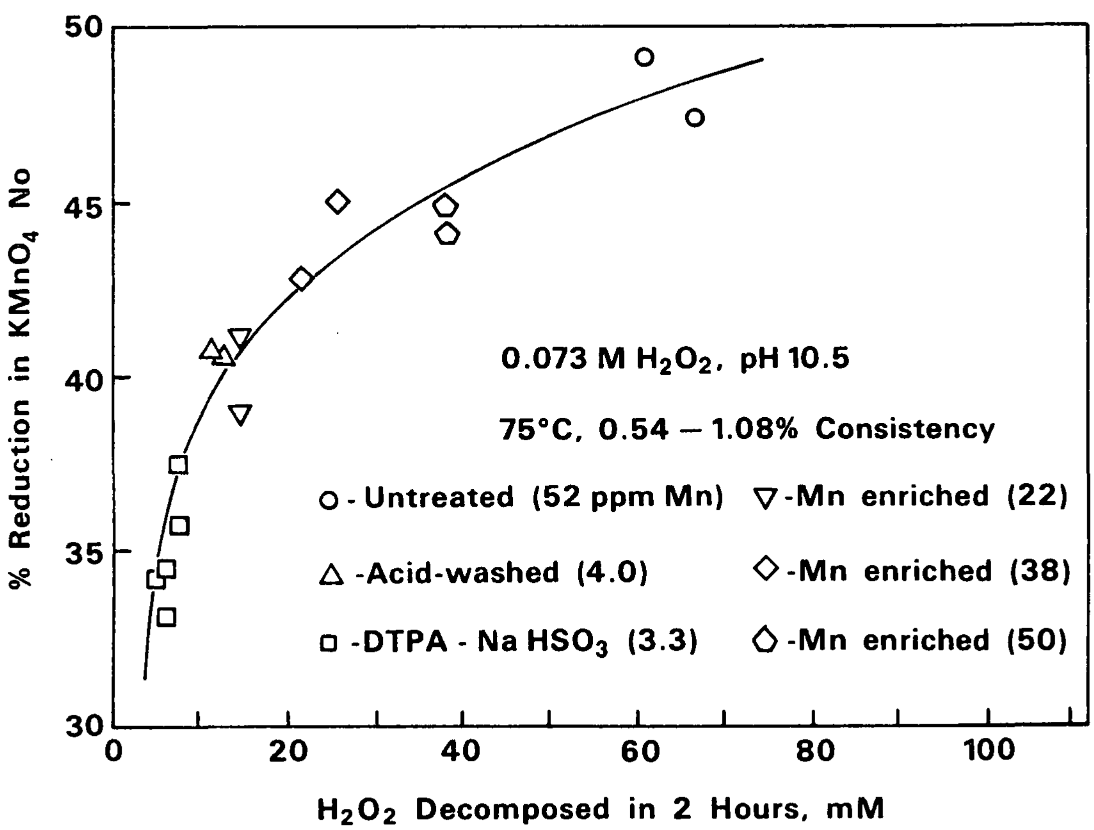
Effects of added metal ions on the degradation of MBB (a residual-lignin model compound) in alkaline hydrogen peroxide (initial pH 11.0, $[H_2O_2]_o$ = 100 nM, 45°C).



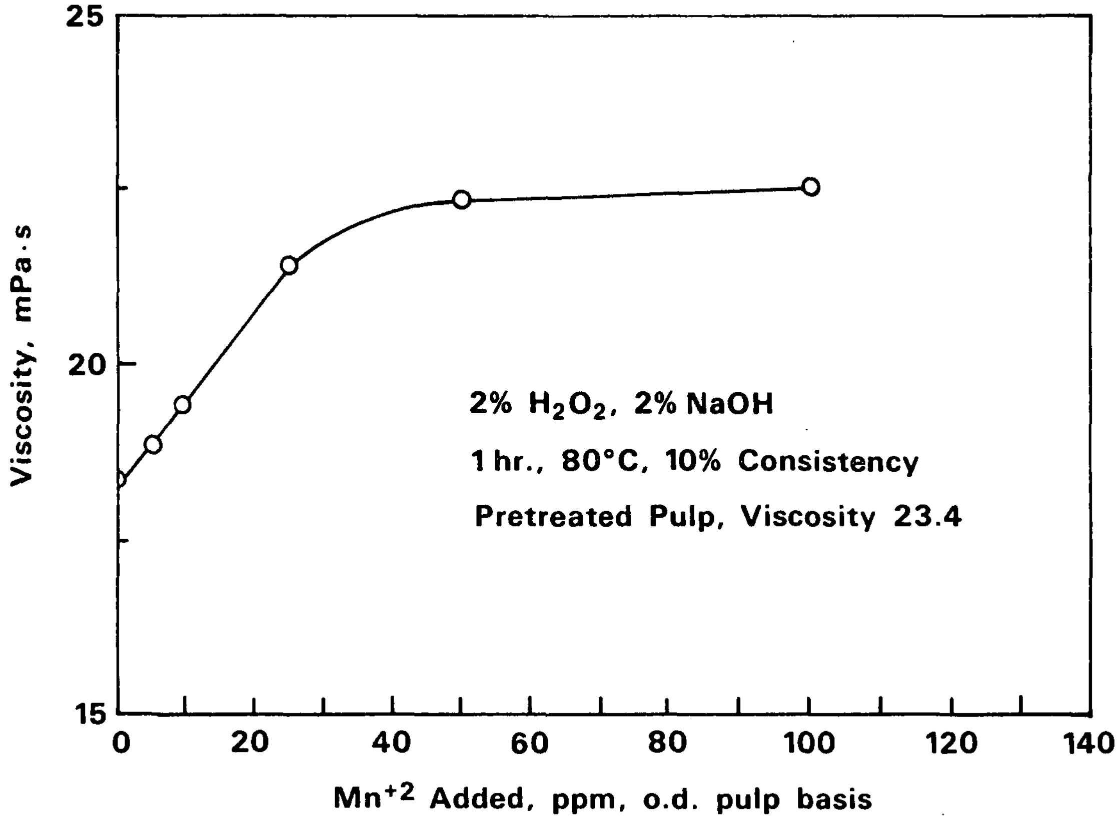
Influence of metal ions on the amount of peroxide decomposition corresponding to a given degree of degradation of MBB, a residual-lignin model compound.



Effect of Peroxide Stabilization on Delignification Rate.



Effect of manipularing the peroxide decomposition rate on the delignification rate.



Effect of manganese addition on viscosity retention during peroxide delignification.

SULFITE-ANTHRAQUINONE KINETICS

- ANALYSIS OF EXISTING DATA FOR 1987 PULPING CONFERENCE PAPER
- PH.D. THESIS (KARYN SIME)

CHLORINATION KINETICS

(PH.D. THESIS RESEARCH)

- LOW CONSISTENCY: SEBASTIAN PUGLIESE
- MEDIUM CONSISTENCY: BARBARA BURNS

DIRECTIONS

- MECHANISM OF NO_2 EFFECT
- ALTERNATIVES TO NO_2
- PEROXIDE DELIGNIFICATION
  - STUDENT RESEARCH
- SULFITE-AQ KINETICS
  - REPORTING
  - STUDENT RESEARCH
- CHLORINATION KINETICS
  - STUDENT RESEARCH

Project 3524

Earl Malcolm

PROJECT 3524
FUNDAMENTALS OF BRIGHTNESS STABILITY

OBJECTIVE:

DEFINE MECHANISM OF YELLOWING ON EXPOSURE TO LIGHT OF HIGH YIELD PULP

STAFF RESEARCH (MALCOLM)

STUDENT (LEBO)

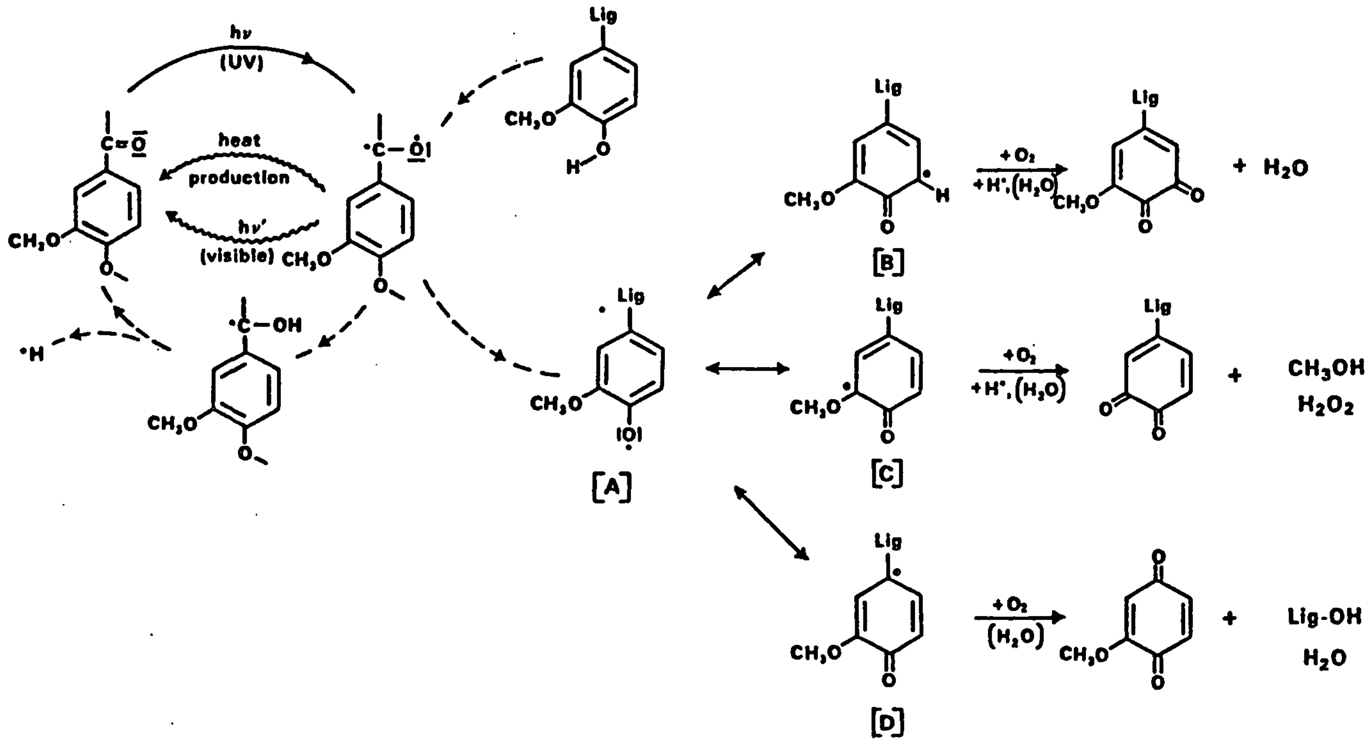


Figure 10. The mechanism of the light-induced yellowing reaction of high-yield pulps.

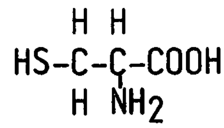
MECHANISTIC PROBES

CHEMICAL TREATMENT

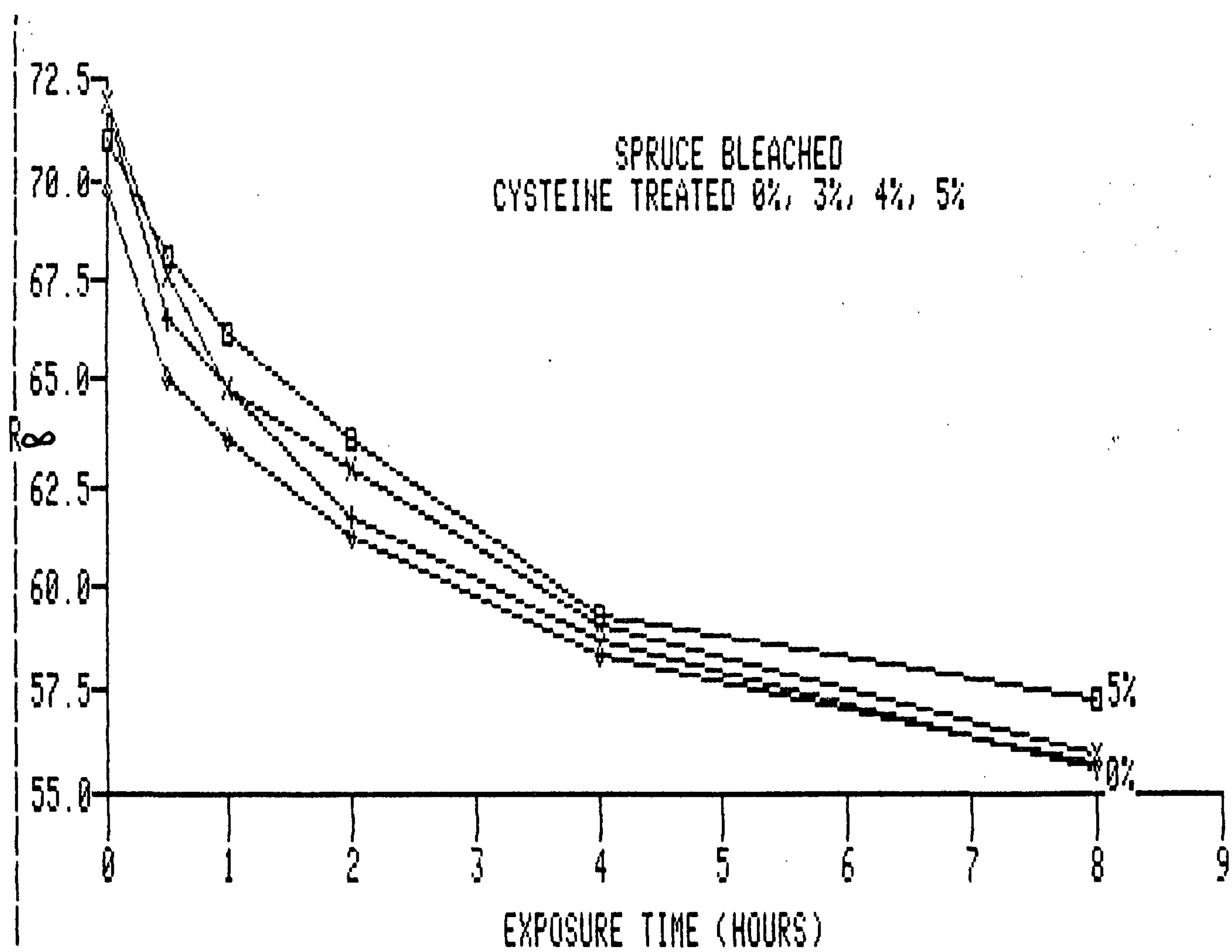
CYSTEINE

METHYLATION

ACETYLATION

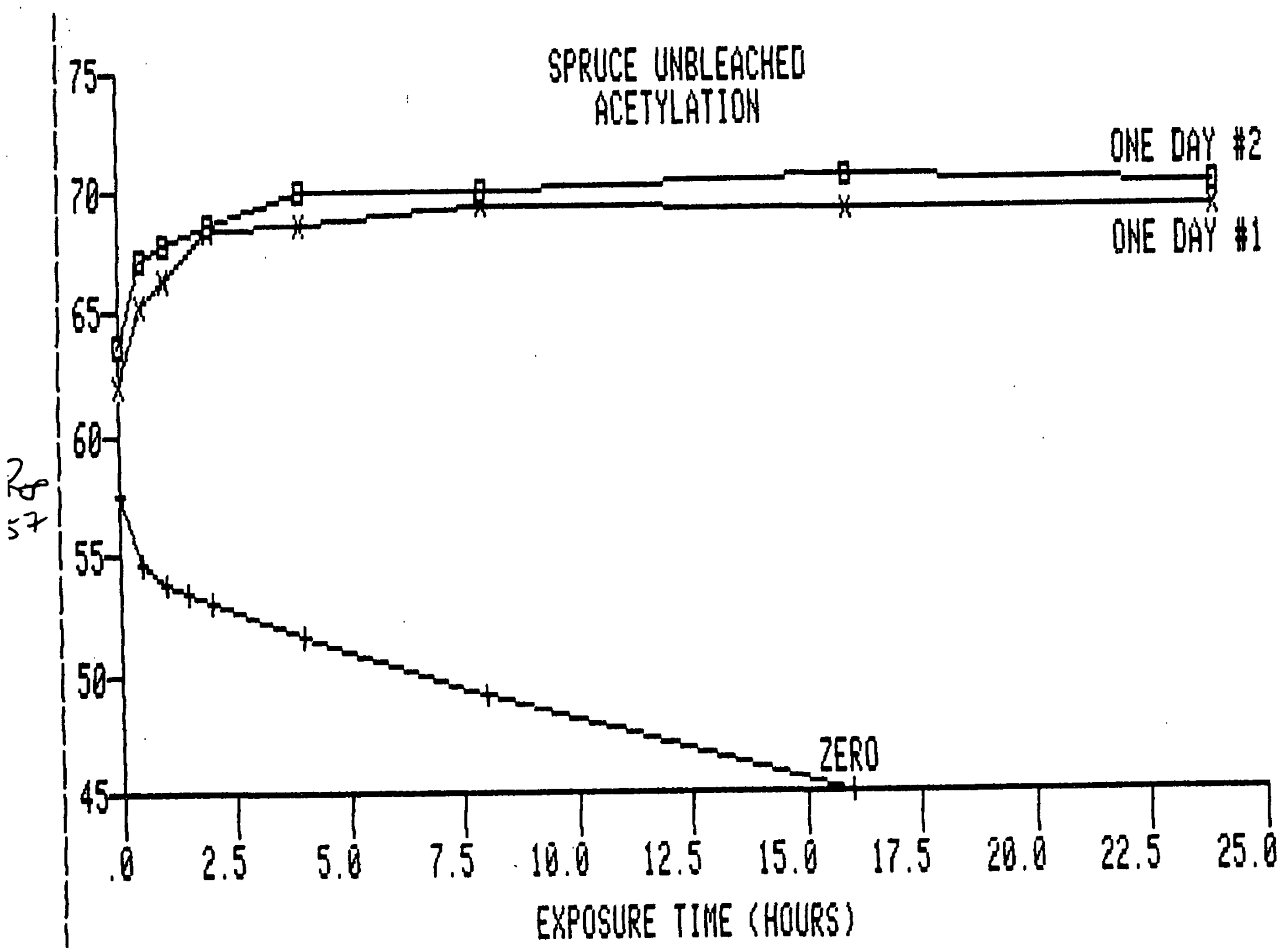

H H
HS-C-C-COOH
H NH2

CYSTEINE


SPRUCE BLEACHED
CYSTEINE TREATED 0%, 3%, 4%, 5%
R∞
72.5
70.0
67.5
65.0
62.5
60.0
57.5
55.0
0
1
2
3
4
5
6
7
8
9
5%
0%
EXPOSURE TIME (HOURS)

	CONTROL	TREATED
~~BLACK~~ ASPEN	77 ——> 71	78.5 ——> 71.5
BLACK SPRUCE	74 ——> 66	76.7 ——> 69.8

EFFECT OF METHYLATION ON BRIGHTNESS CHANGE AFTER 4-HOUR LIGHT EXPOSURE

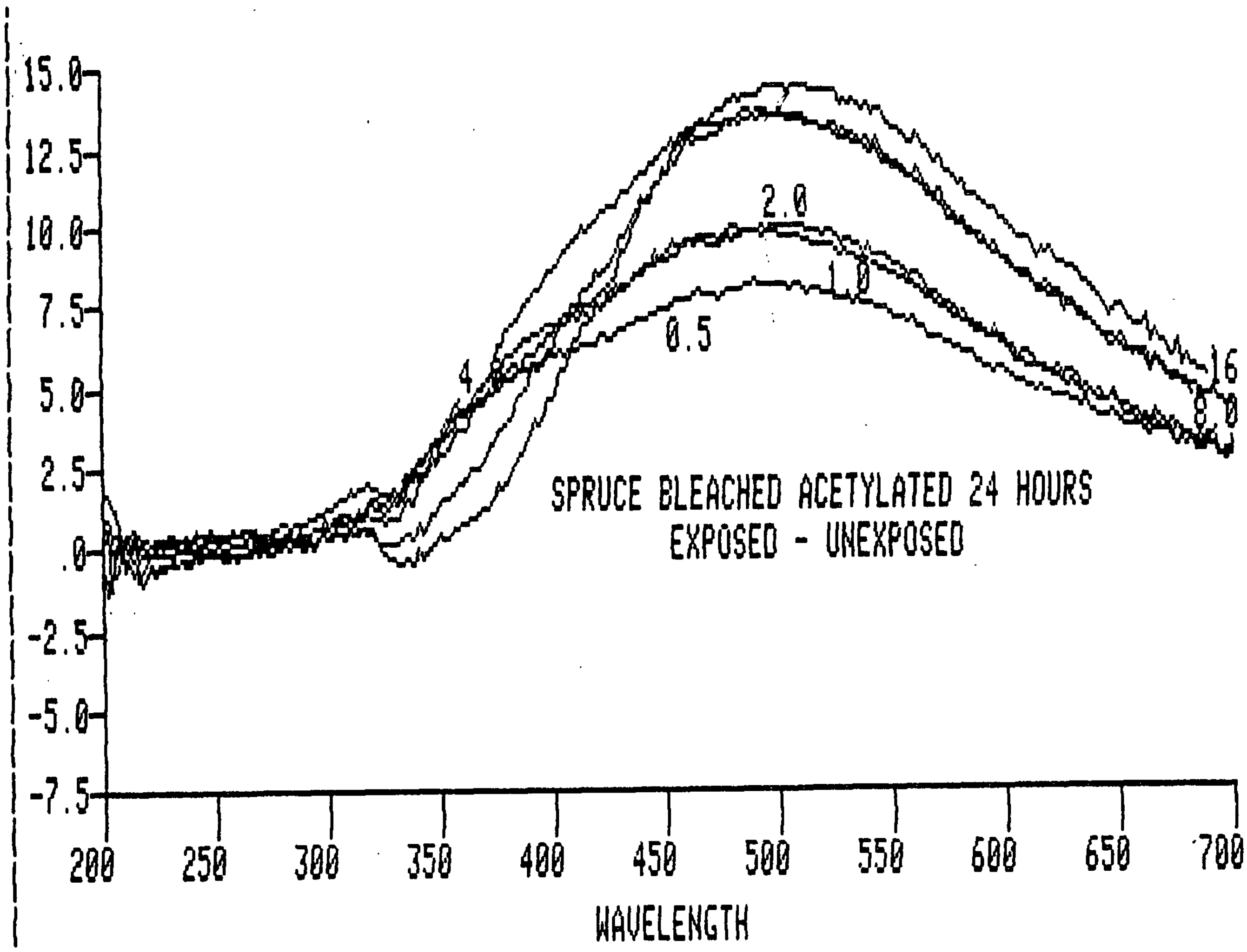


EFFECT OF ACETYLATION ON YELLOWING

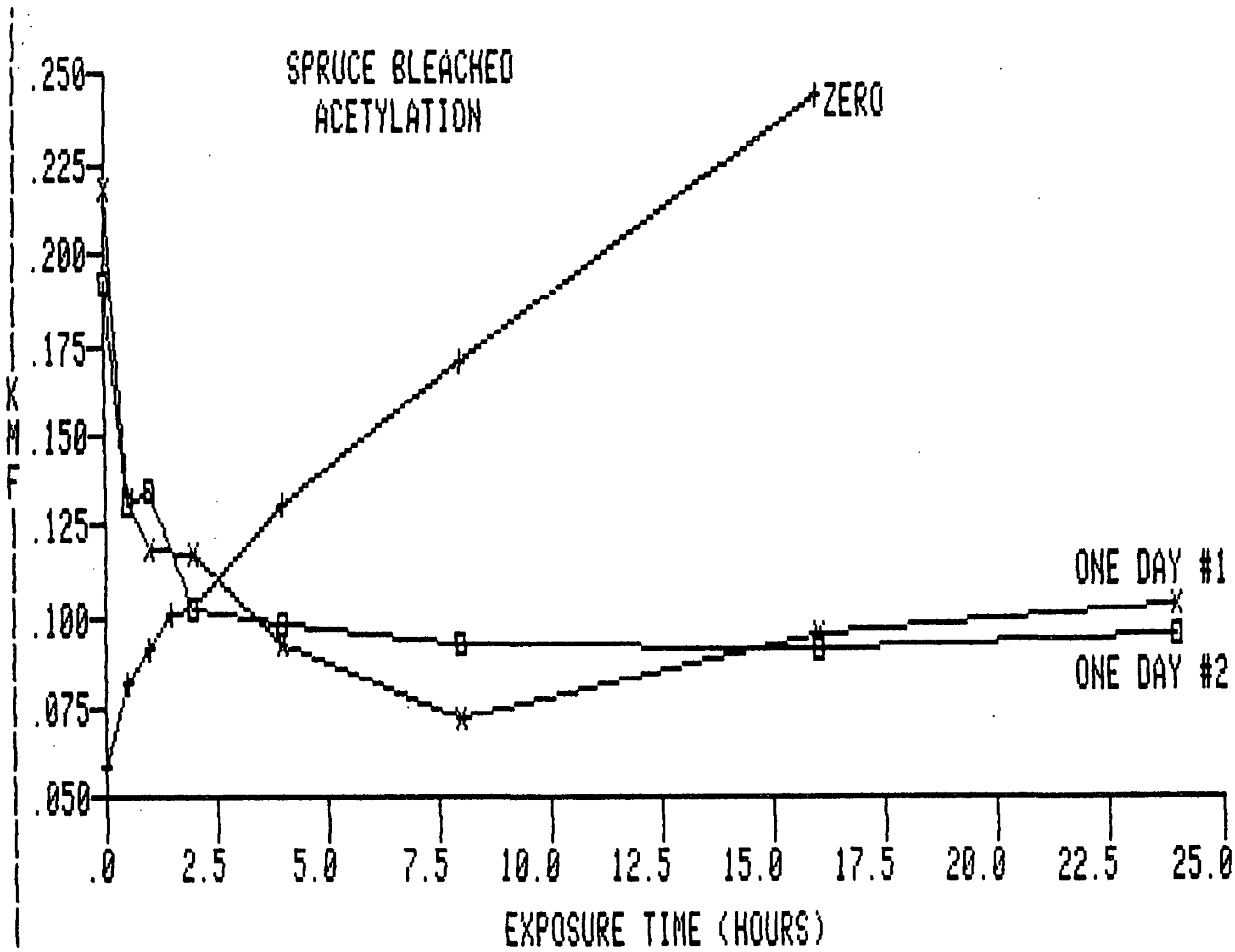
alkali extract bs + NaOH

buffer

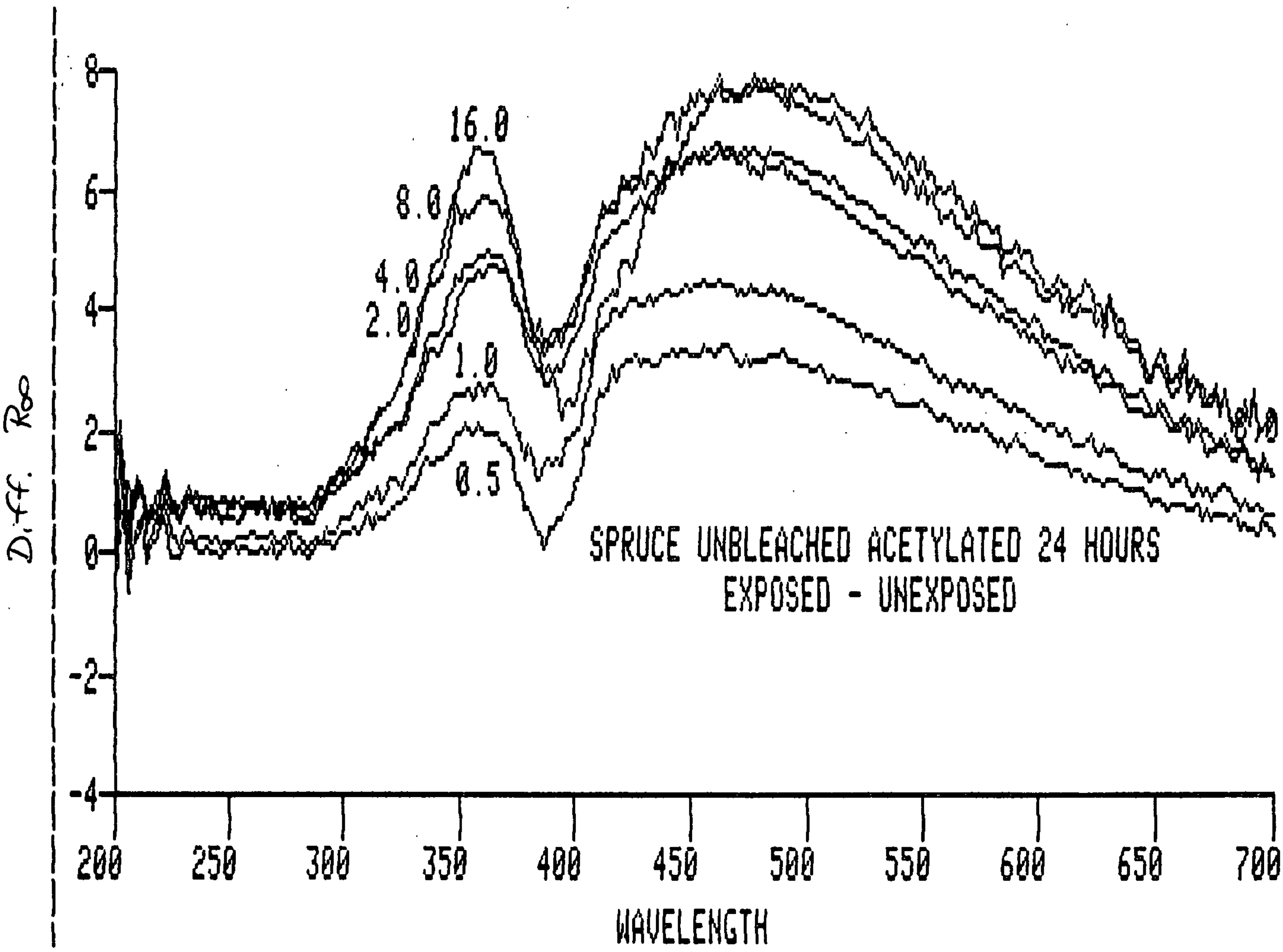
$40°$ + $NaHCO_3$ + Na_2CO_3



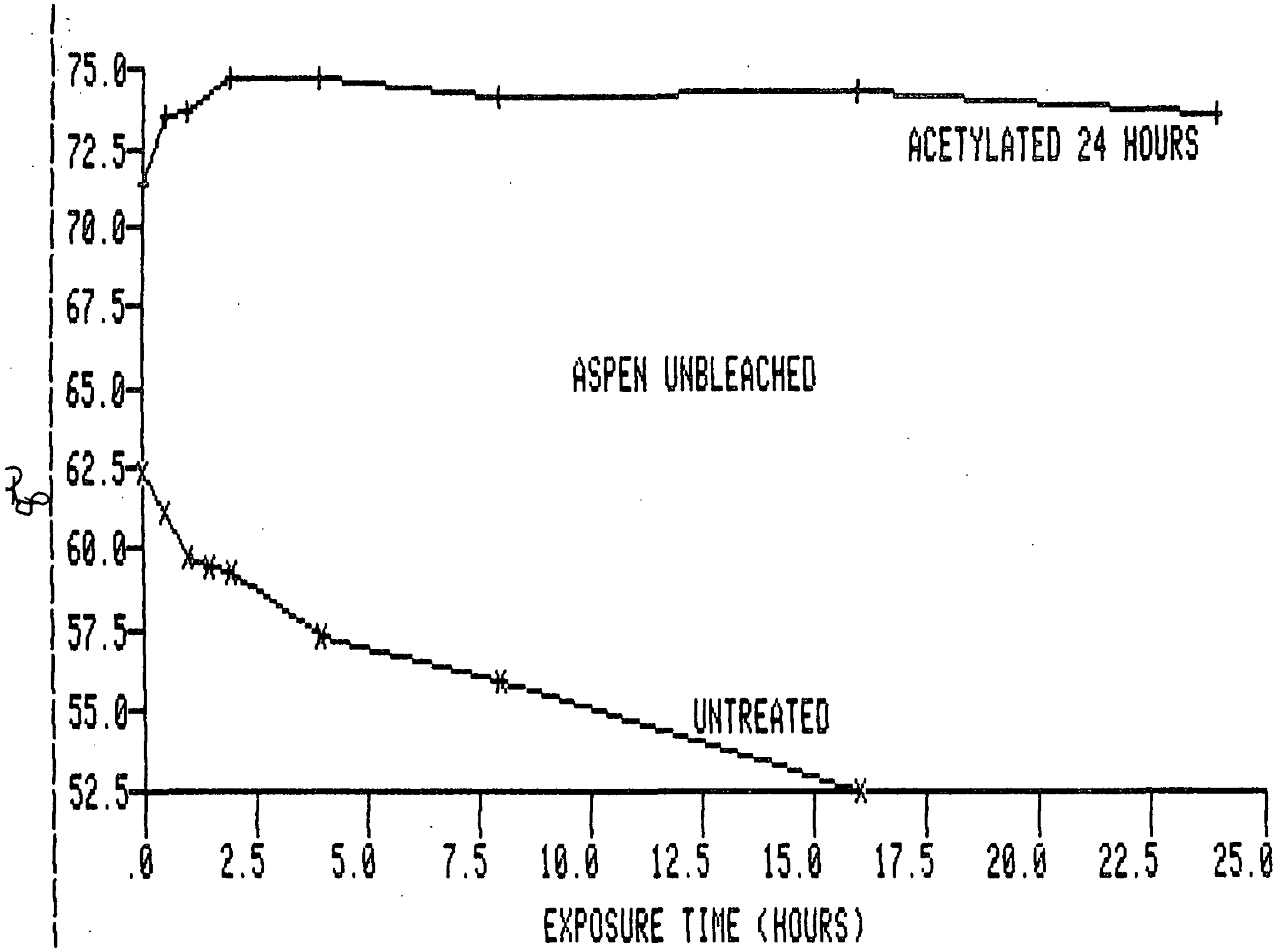
EFFECT OF ACETYLATION ON YELLOWING



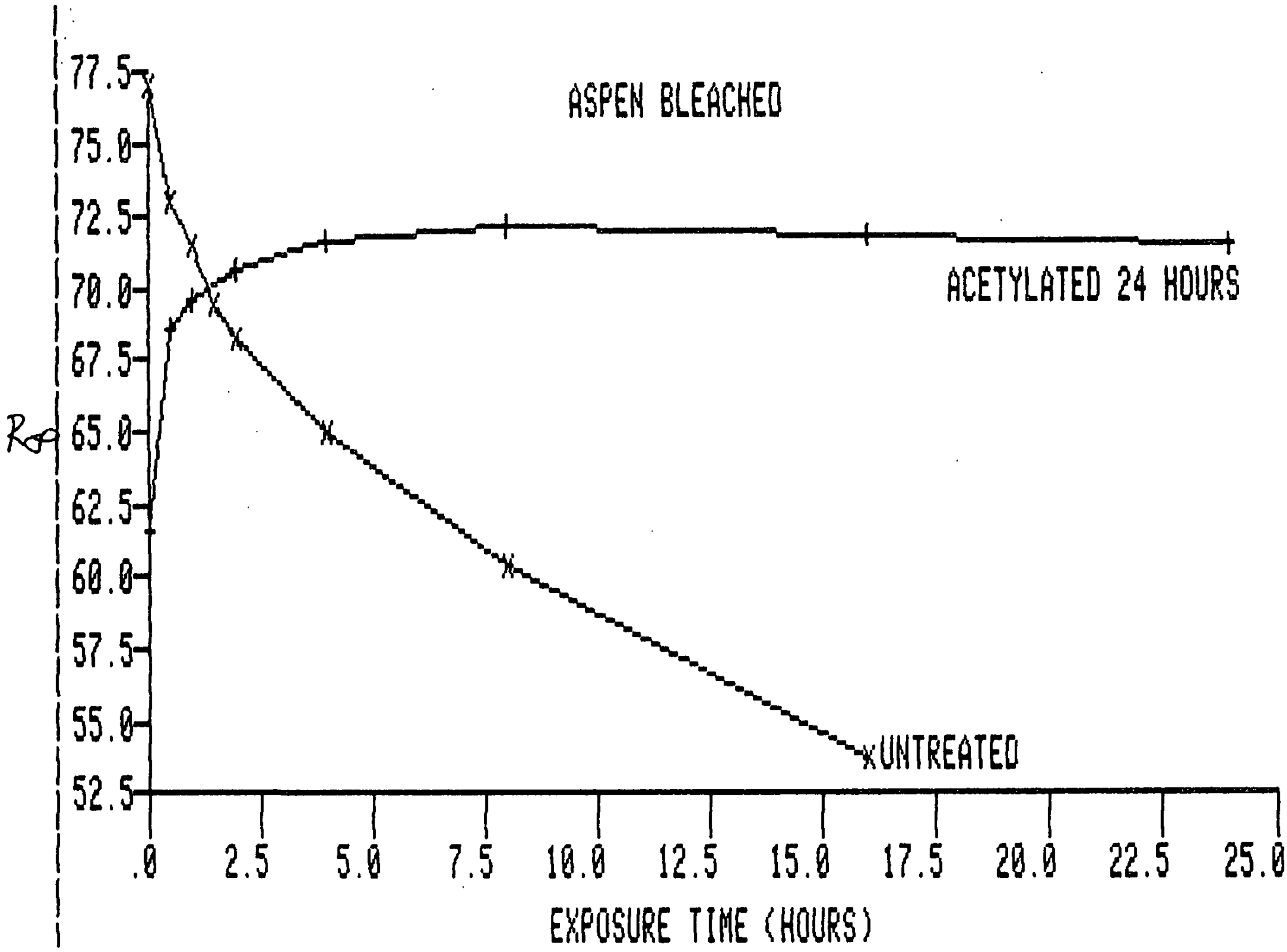
Effect of Acetylation on Yellowing



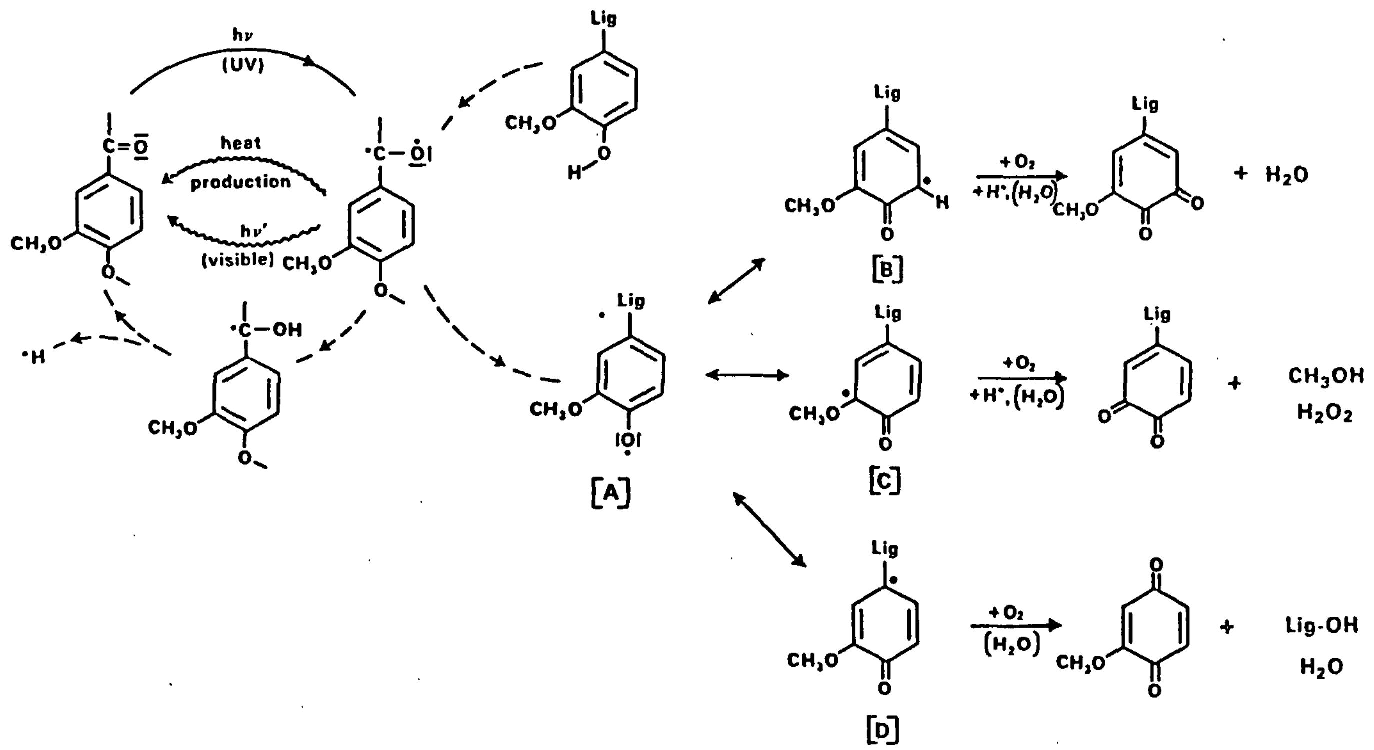
EFFECT OF ACETYLATION ON YELLOWING



Effect of Acetylation on Yellowing



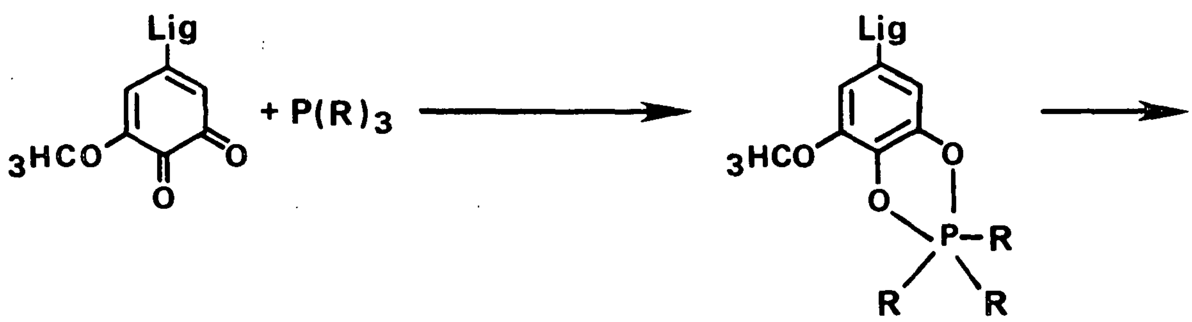
EFFECT OF ACETYLATION ON YELLOWING



The mechanism of the light-induced yellowing reaction of high yield pulps.

Analytical Methods Used to Qualitatively Show the Formation of Quinonoid Lignin Structures

Trivalent Phosphorous Compounds

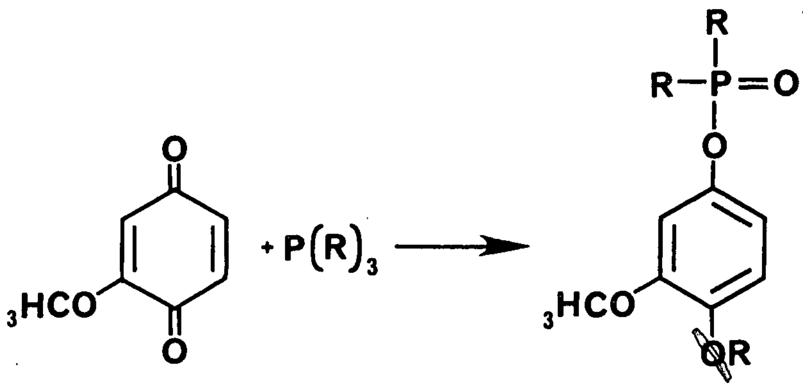


R = alkyl in phosphines (i.e.CH_3, C_2H_5)

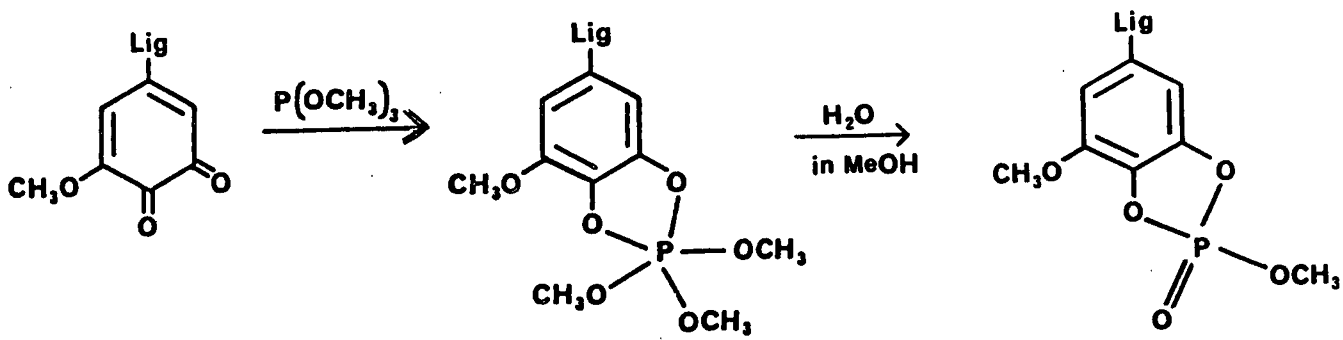
R = a R = alkoxyl in phosphites (i.e. OCH_3, OC_2H_5)

Analytical Methods Used to Qualitatively Show the Formation of Quinonoid Lignin Structures

Trivalent Phosphorous Compounds



R = alkoxyl in phosphites (i.e. OCH_3, OC_2H_5)



(Stuart Lebo, PhD thesis)

Oxidation of Expected Oxyphosphorane Structures to
Cyclic Phosphates by Air or Water.

SUMMARY OF SOLID STATE ^{31}P NMR ANALYSIS: METHANOL EXPERIMENTS

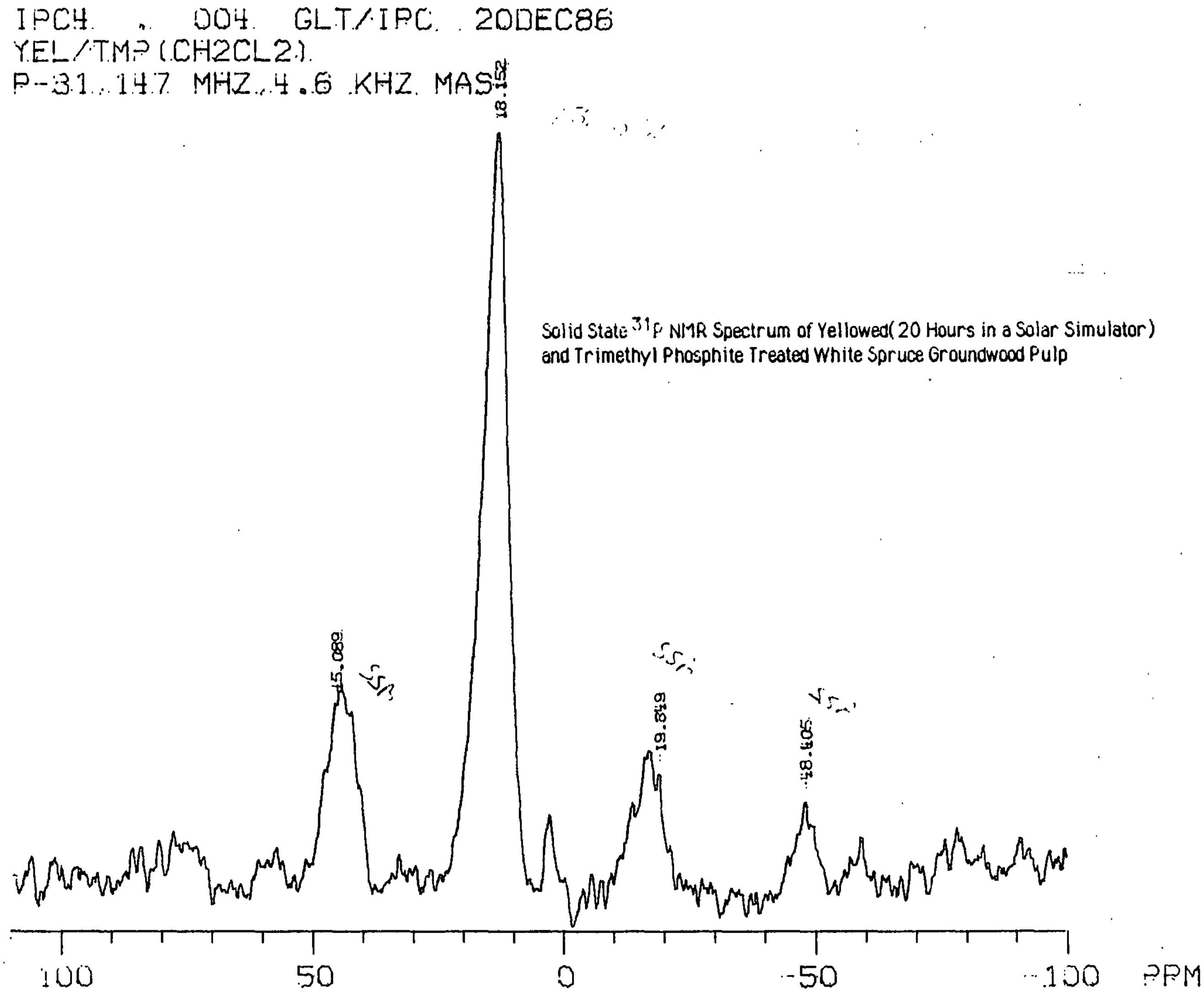
Sample I. D.	Treatment Time (days)	Observed Signals* (ppm)	Relative Area (%)
Untreated pulp	7	13.6	85.1
		10.4	14.9
Yellowed Pulp**	7	12.7	71.6
		10.2	7.0
		3.4	21.4
Fremy's Salt pulp***	7	13.6	40.9
		10.7	12.6
		5.5	46.5
Cellulose****	7	13.6	
		-4.5	

* versus 85% H_3PO_4

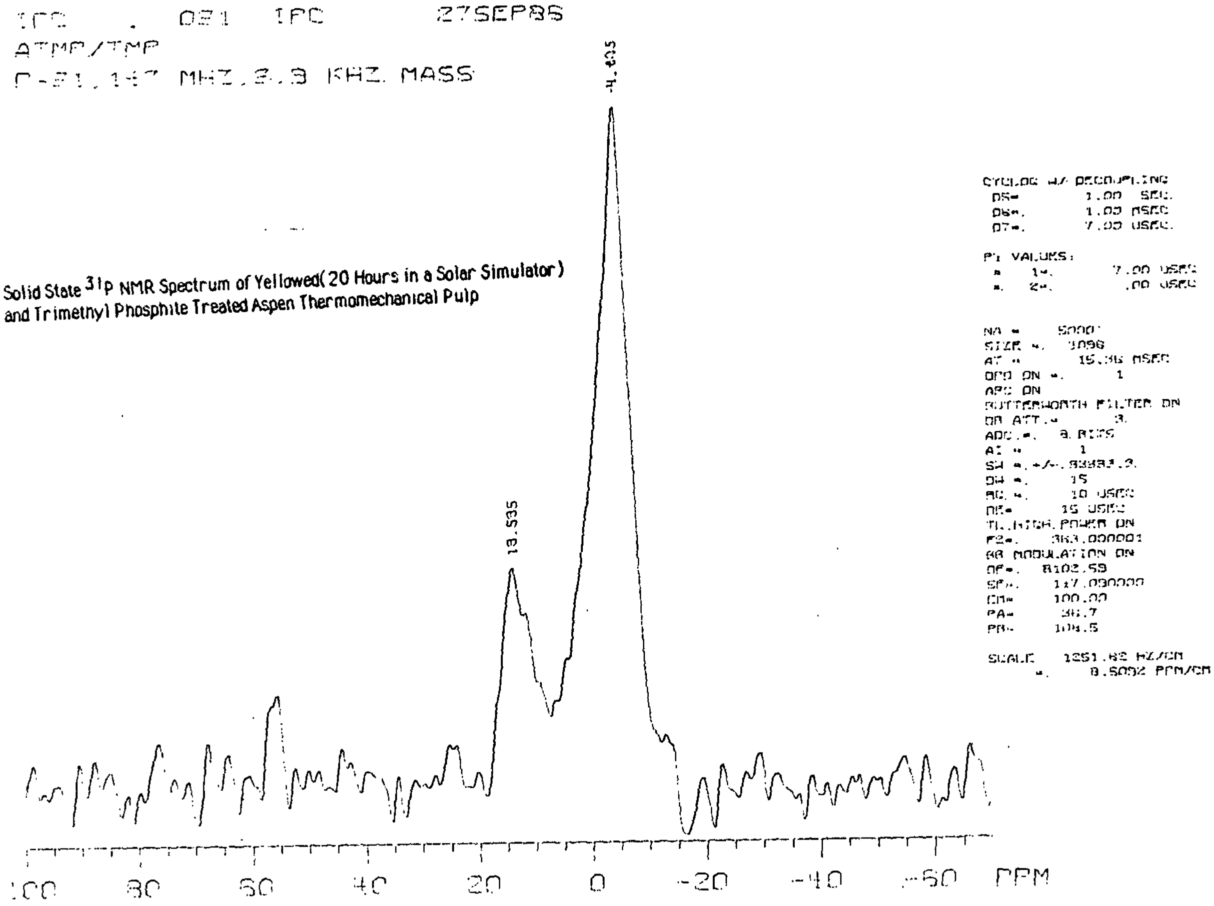
** 20 hours in the solar simulator operating at 990 Watts

*** model pulp

**** Whatman No. 1 Sheets



Solid State ^{31}P NMR Spectrum of Yellowed(20 Hours in a Solar Simulator) and Trimethyl Phosphite Treated White Spruce Groundwood Pulp

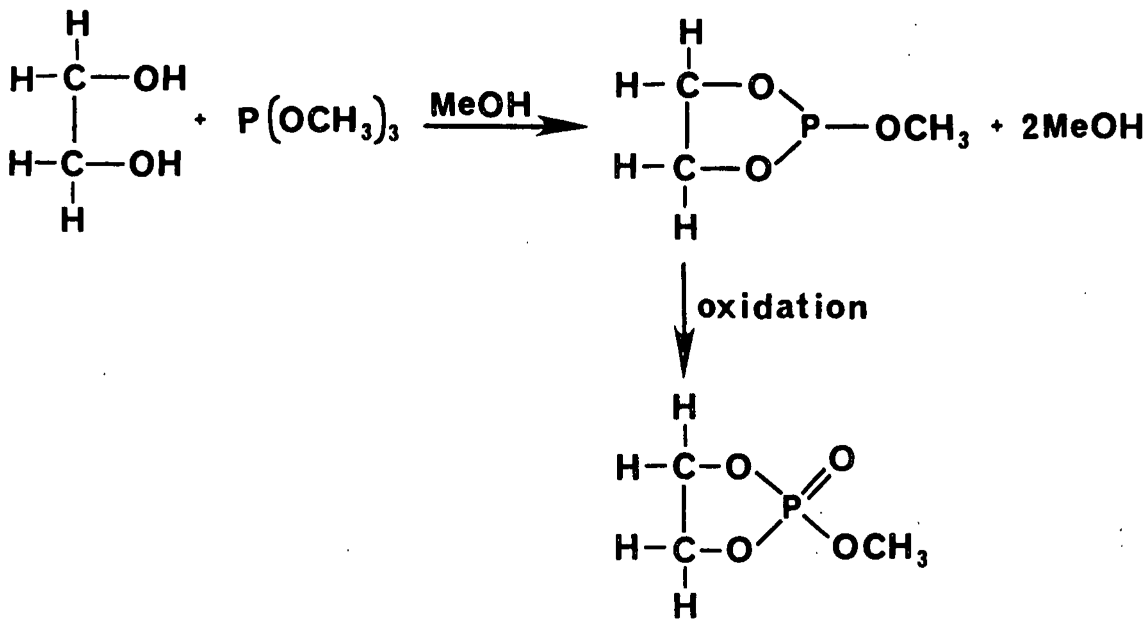


Solid State ^{31}P NMR Spectrum of Yellowed (20 Hours in a Solar Simulator) and Trimethyl Phosphite Treated Aspen Thermomechanical Pulp

SUMMARY OF PHOSPHORUS MICROANALYSIS RESULTS: METHANOL EXPERIMENTS

Sample I.D.	Treatment Time (days)	Average %P (g P/g o.d. pulp)	Number of Determinations	Standard Deviation
Untreated Pulp	7	0.330	9	0.169
Yellowed Pulp*	7	0.799	9	0.222
Cellulose**	1	0.110	3	0.011
	3	0.120	3	0.006
	7	0.090	3	0.006

*20 hours in the solar simulator operating at 990 Watts
**Whatman No. 1 Sheets



Possible Mechanism for the Formation of Cyclic Phosphate Structures from Cellulose.

SUMMARY OF SOLID STATE ^{31}P NMR ANALYSIS: CH_2Cl_2 EXPERIMENTS

Sample I.D.	Treatment Time (days)	Observed Signals* (ppm)	Relative Area (%)
Untreated pulp-1	7	12.6 4.4	66.5 33.5
Untreated pulp-2	7	12.5 5.6	78.0 22.0
Untreated pulp-3	7	13.6 2.5	70.0 3.7
Yellowed Pulp**	7	12.6 2.1	94.9 5.1
Fremy's Salt pulp***	7	13.5	100
Cellulose****	7	≈ 13	very weak
Holocellulose*****	7	≈ 13	very weak

* versus 85% H_3PO_4

** 20 hours in the solar simulator operating at 990 Watts

*** model pulp

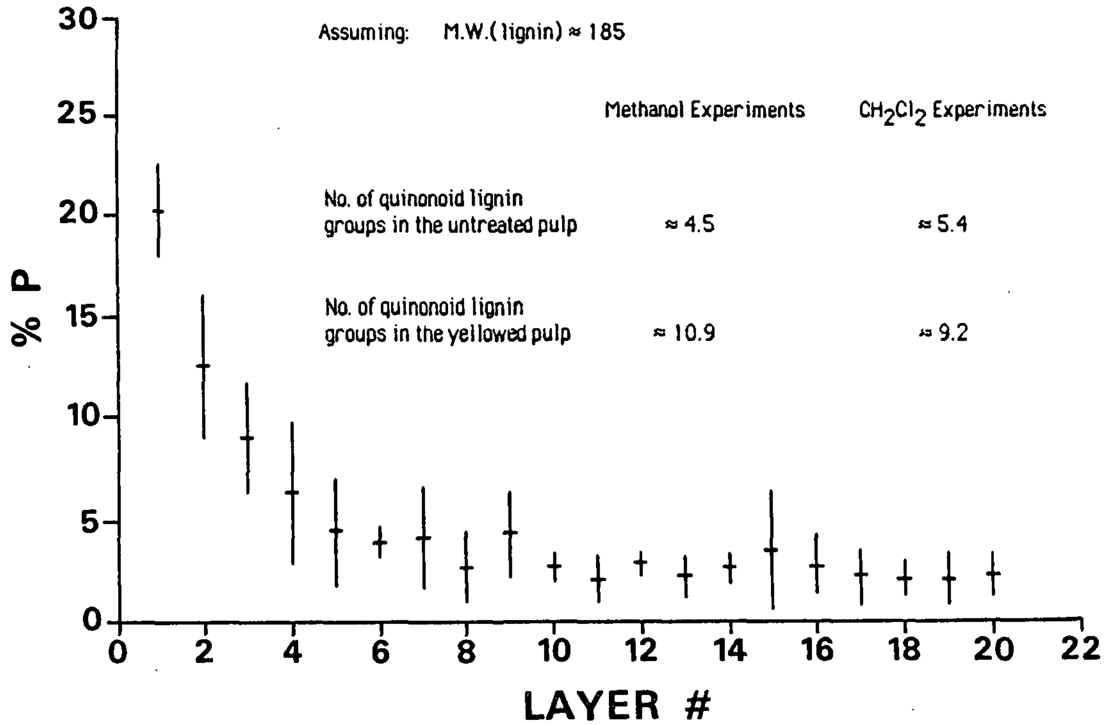
**** Whatman No. 1 Sheets

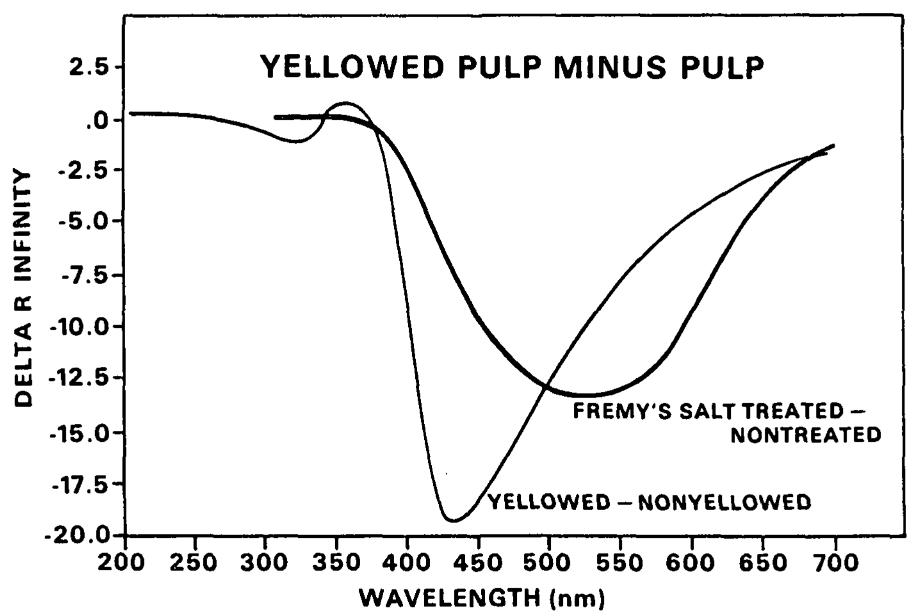
***** acid chlorite prepared; Klason lignin = 1.5%

SUMMARY OF PHOSPHORUS MICROANALYSIS RESULTS: CH_2CL_2 EXPERIMENTS

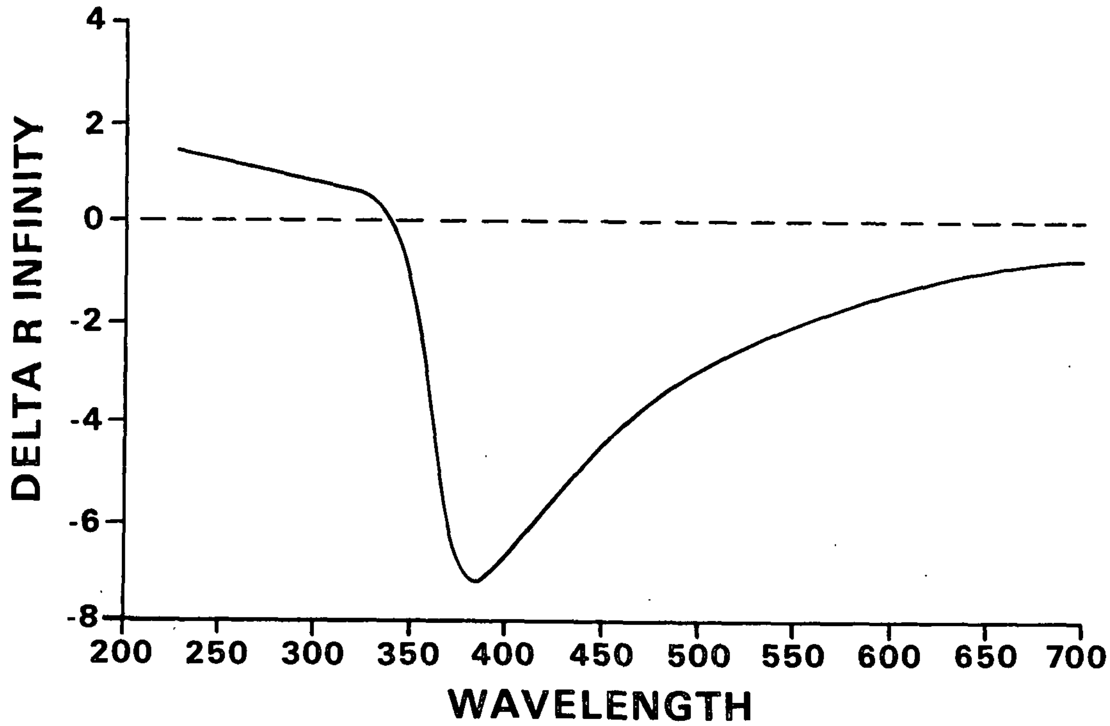
Sample I. D.	Treatment Time (days)	Average %P(g P/g pulp) Run #1	Run #2
Untreated Pulp-1	7	0.49	0.45
Untreated Pulp-2	7	0.40	0.40
Untreated Pulp-3	7	0.47	0.48
Untreated Pulp-4	7	0.29	0.30
Yellowed Pulp*	7	0.48	0.46
Fremy's Salt Pulp**	7	0.46	0.47
Cellulose***	7	0.06	0.05
Holocellulose****	7	0.05	0.05

* 20 hours in the solar simulator at 990 Watts
** model pulp
*** Whatman No. 1 filter paper
**** acid chlorite prepared; Klason lignin = 1.5%

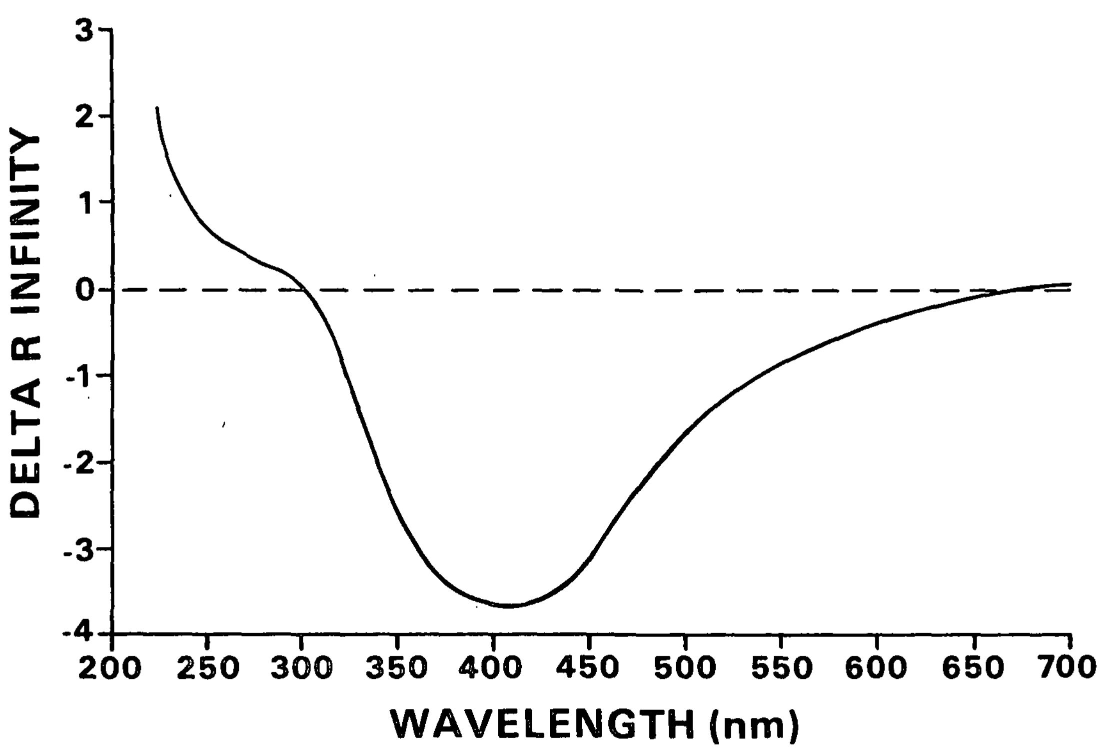




Difference Spectra Obtained by Subtracting the Refelctance Spectrum of a White Spruce Groundwood Pulp from the Reflectance Spectra of Yellowed and Fremy's Salt Treated White Spruce Groundwood Pulp



Difference Spectrum Obtained by Subtracting the Reflectance Spectrum of an Acid Chlorite White Spruce Holocellulose from the Reflectance Spectrum of an Acid Chlorite White Spruce Holocellulose Yellowed for 2 Hours in a Solar Simulator



Difference Spectrum Obtained by Subtracting the Reflectance Spectrum of an Isolated Spruce Glucomannan from the Reflectance Spectrum of the Same Glucomannan Yellowed for 2 Hours in a Solar Simulator

Project 3566

Tom McDonough

N_2O_4 + TMP + O_2-NaOH

Br_2 + TMP + O_2-NaOH

N_2O_4 + Br_2 + TMP + O_2-NaOH

PROJECT 3566

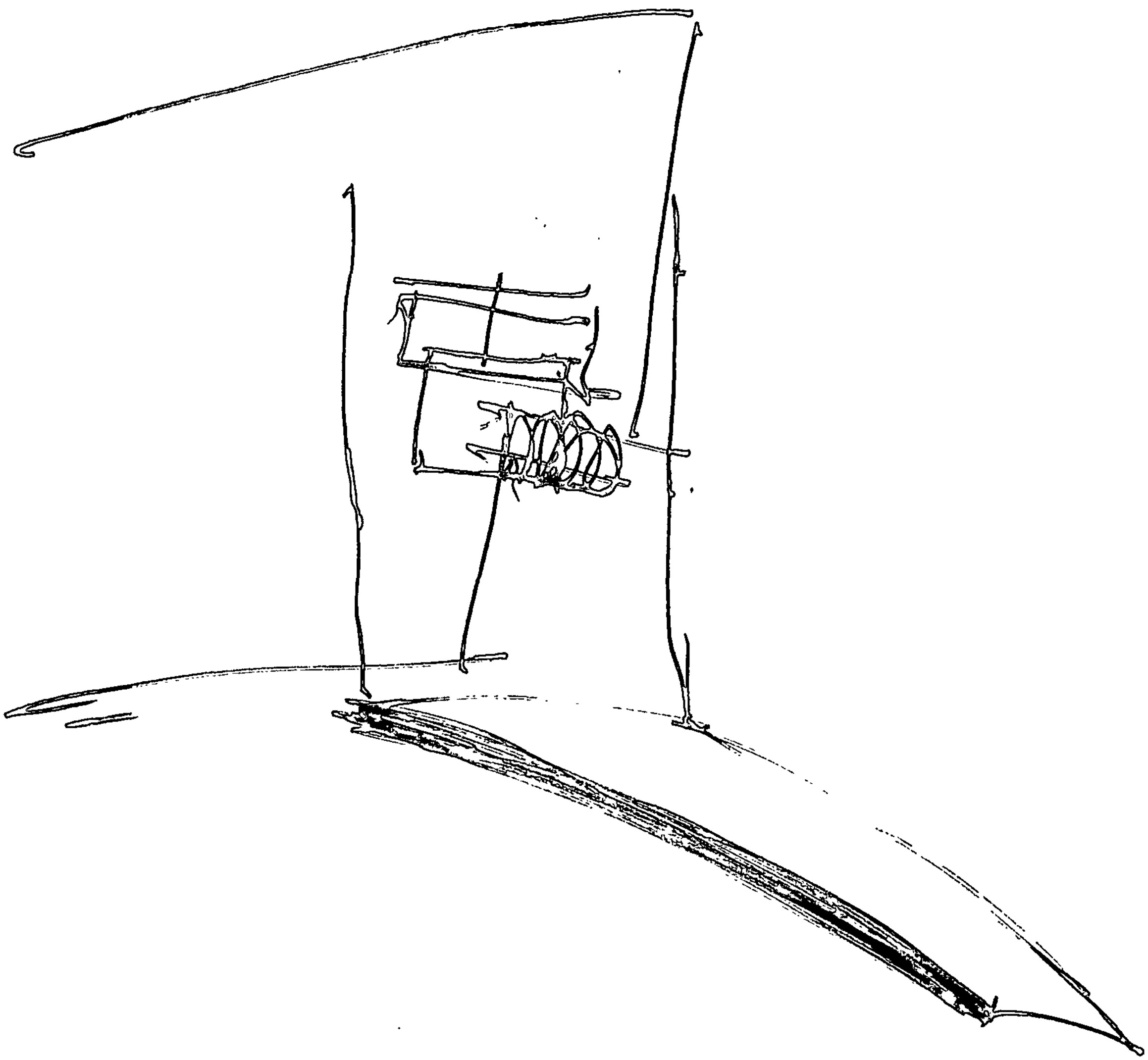
SEPARATION OF STRONG, INTACT FIBERS

OBJECTIVE

MINIMIZE THE CHANGES IN FIBER STRENGTH AND GEOMETRY WHICH ACCOMPANY FIBER SEPARATION

FIBER ATTRIBUTES NEEDED TO MAKE STRONG PAPER

- LENGTH
- STRENGTH
- COMFORMABILITY
- ACTIVE BONDING SURFACE



Relevant Questions

- How long and strong are the fibers in wood?
- How long and strong are the fibers in kraft pulp?
- How long and strong are the fibers in high yield pulp made under standard conditions?
- How can high yield pulping conditions be changed to minimize effects on fiber length and strength?

Relevant Questions

- Can strong high yield fibers be bonded together to form a sheet in which a fiber number disadvantage relative to kraft is largely or completely compensated for by a fiber strength advantage?
- To what extent are the answers to the above questions dependent on species?
- Can the strength of a wood fiber be increased beyond its native value?

PILOT SCALE DISK REFINER FIBERIZATION OF WHITE SPRUCE

Sample Identity	Presteaming Vessel Temperature, °C	Primary Refiner Plate Clearance, mm	Specific Energy Consumption HPD/T	0.014" Cut Screen Rejects, %	0.006" Cut Screen Rejects, %
775-1	29	0.80	55.7	12.9	44.4
775-2	57	0.80	48.0	15.0	59.5
773-1	120	0.40	21.4	2.8	50.4
773-2	121	0.40	22.6	4.7	55.8
774-1	160	0.60	7.6	11.2	61.3
774-2	160	0.60	10.2	12.1	58.9

CLASSIFICATION OF FIBROUS FRACTION OF

REFINER-FIBERIZED WHITE SPRUCE

Sample Identity	Presteaming Vessel Temperature, °C	% Retained on Screen of Mesh Size				
		14	28	48	100	Remainder
775-1	29	4	30	27	15	24
775-2	57	7	37	31	13	13
773-1	120	27	33	18	5	16
773-2	121	24	37	21	6	12
774-1	160	20	37	20	6	16
774-2	160	22	43	20	7	9

LENGTH OF FIBERS IN REFINER-FIBERIZED WHITE SPRUCE

Sample Identity	Presteaming Vessel Temparature, °C	Weighted Average Length of Fibers in Whole Pulp	28 Mesh Fraction	48 Mesh Fraction	100 Mesh Fraction
775-1	29	0.96	N.D.*	1.40	0.75
775-2	57	1.26	2.18	1.31	0.77
773-1	120	1.73	2.35	1.47	0.83
773-2	121	1.68	2.42	1.42	0.84
774-1	160	1.96	N.D.	1.60	0.88
774-2	160	1.76	N.D.	1.51	0.91

* N.D. - NOT DETERMINED.

PROPERTIES OF HANDSHEETS MADE FROM FIBROUS FRACTION

OF REFINER-FIBERIZED WHITE SPRUCE

Sample Identity	Presteaming Vessel Temperature, °C	Disintegration Time, Min.	C.S.F., mL	Zero Span B.L., km	Tensile Index N.m/g	Burst Index kPam²/g	Tear Factor	Density g/cm³
775-1	29	0	750	6.9	3.8	N.M.*	16.3	0.17
775-2	57	0	N.D.**	6.9	2.4	N.M.	16.2	0.14
773-1	120	0	760	6.8	0.7	N.M.	9.6	0.13
773-2	121	0	N.D.	6.1	0.7	N.M.	10.5	0.12
774-1	160	0	750	5.5	0.4	N.M.	9.1	0.13
774-2	160	0	N.D.	6.5	0.6	N.M.	8.1	0.14

* N.M. - Not measurable.
**N.D. - Not determined.

PROPERTIES OF HANDSHEETS MADE FROM FIBROUS FRACTION

OF REFINER-FIBERIZED WHITE SPRUCE

Sample Identity	Presteaming Vessel Temperature, °C	Disintegration Time, Min.	C.S.F., mL	Zero Span B.L., km	Tensile Index N.m/g	Burst Index kPam^2/g	Tear Factor	Density g/cm^3
775-1	29	180	350	8.9	22.4	1.2	53	0.21
775-2	57	180	N.D.**	8.7	24.7	1.2	55	0.23
773-1	120	180	660	7.7	13.1	0.7	60	0.17
773-2	121	180	N.D.	7.6	14.4	0.7	49	0.17
774-1	160	180	720	7.1	12.4	N.M.*	41	0.18
774-2	160	180	N.D.	7.8	12.2	0.6	50	0.19

* N.M. - Not measurable.
**N.D. - Not determined.

PINE SINGLE FIBER PROPERTIES
AND THEIR STANDARD ERRORS

Pulp	Load,	Area, mm^2	Stress, kg/mm^2	Modulus, kg/mm^2
RMP	32 ± 2	580 ± 35	59 ± 4	1100 ± 135
CMP	34 ± 2	590 ± 30	59 ± 2	1350 ± 80
BK*	15 ± 1	250 ± 20	62 ± 3	580 ± 30
UBK	22 ± 3	250 ± 20	86 ± 9	1040 ± 140

* Commercial Bleached Kraft

BREAKING LOAD OF INDIVIDUAL FIBERS

FROM REFINER-FIBERIZED WHITE SPRUCE

Sample Identity	Presteaming Vessel Temp., °C	Breaking Load (g) of Fibers From Whole Pulp	14 Mesh Fraction	28 Mesh Fraction	48 Mesh Fraction
775-1	29	18.0	23.4	16.1	13.4
775-2	57	17.1			
773-1	120	13.9	27.0	18.9	10.8
773-2	121	16.4			
774-1	160	16.1			
774-2	160	18.5			
Kraft		17.5			

LSD approximately 3.4

CROSS-SECTIONAL AREA OF INDIVIDUAL FIBERS

FROM REFINER-FIBERIZED WHITE SPRUCE

Sample Identity	Presteaming Vessel Temp., °C	Cross-Sectional Area (μm^2) of Fibers From Whole Pulp	14 Mesh Fraction	28 Mesh Fraction	48 Mesh Fraction
775-1	29	204	239	182	172
775-2	57	186			
773-1	120	209	250	219	161
773-2	121	190			
774-1	160	196			
774-2	160	212			
Kraft		89			

LSD approximately 34

BREAKING STRESS OF INDIVIDUAL FIBERS

FROM REFINER-FIBERIZED WHITE SPRUCE

	Presteaming	Breaking Stress (kg/mm^2) of Fibers From			
Sample Identity	Vessel Temp., °C	Whole Pulp	14 Mesh Fraction	28 Mesh Fraction	48 Mesh Fraction
775-1	29	93	108	94	92
775-2	57	93			
773-1	120	76	111	88	68
773-2	121	90			
774-1	160	91			
774-2	160	89			
Kraft		201			

LSD approximately 20

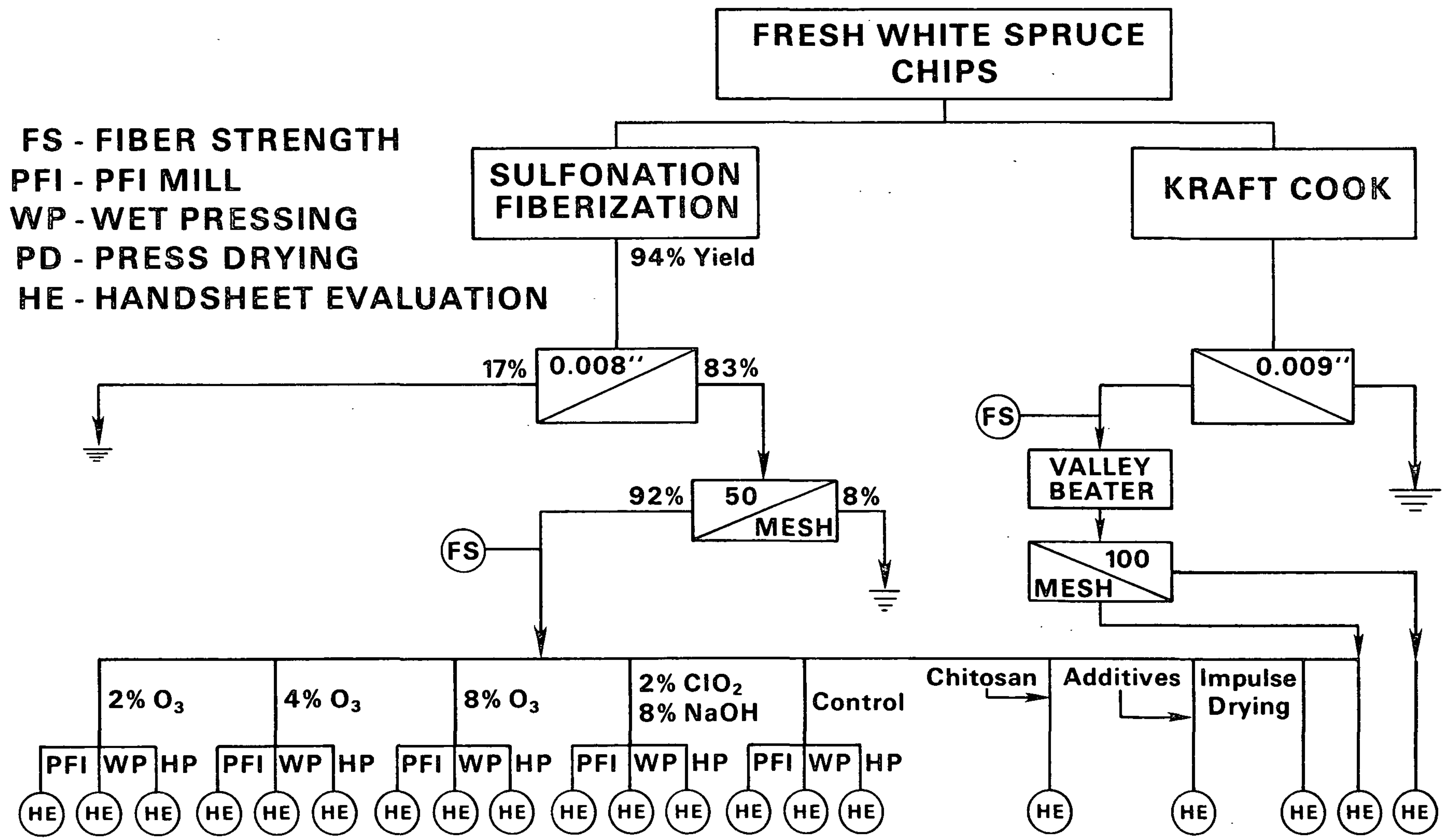
MODULUS OF INDIVIDUAL FIBERS

FROM REFINER-FIBERIZED WHITE SPRUCE

	Presteaming	Modulus (kg/mm^2) of Fibers From			
Sample Identity	Vessel Temp., °C	Whole Pulp	14 Mesh Fraction	28 Mesh Fraction	48 Mesh Fraction
775-1	29	1045	1445	1265	1110
775-2	57	1200			
773-1	120	920	1220	920	765
773-2	121	1060			
774-1	160	1080			
774-2	160	980			
Kraft		3070			

LSD approximately 290.

BONDING STUDIES

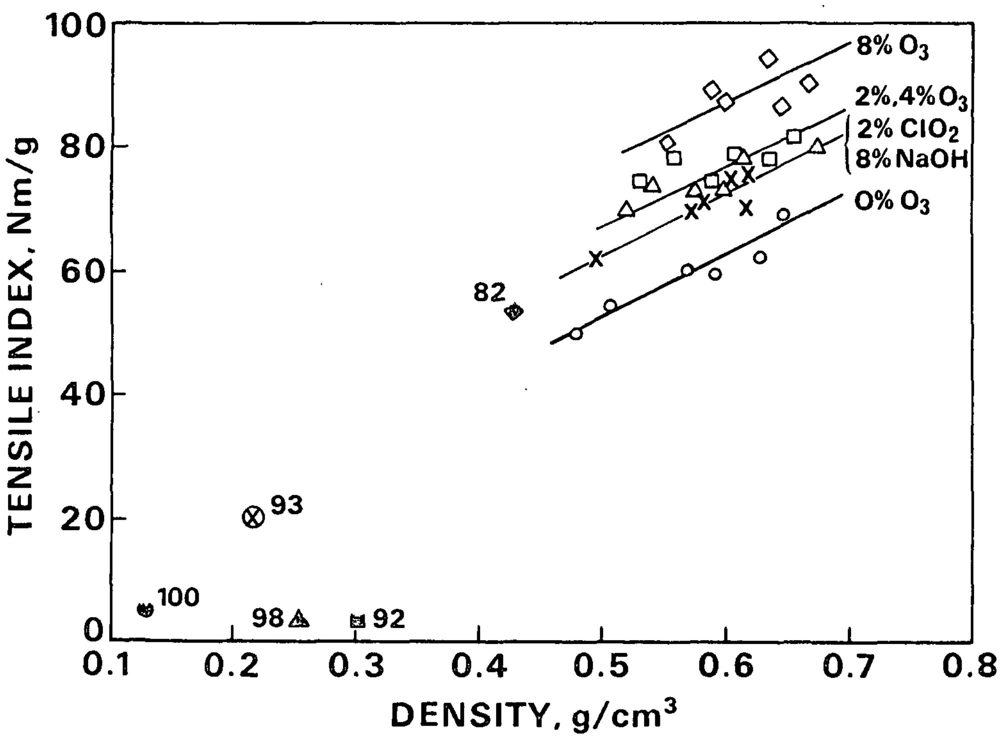


Experimental plan for bonding strong high yield fibers.

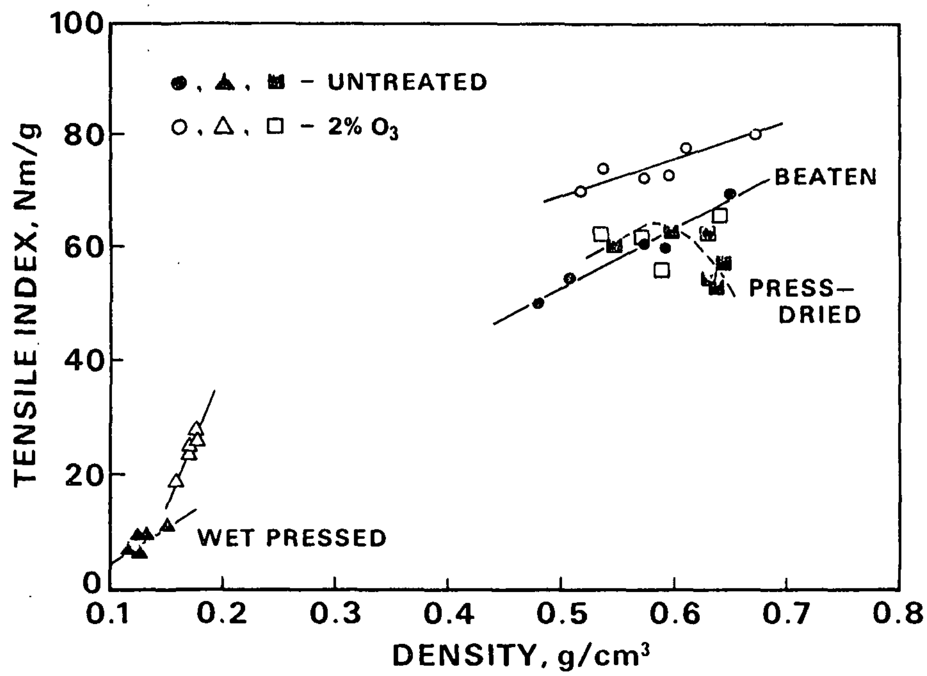
PROPERTIES OF INDIVIDUAL FIBERS FROM

SULFONATED WHITE SPRUCE

PROPERTY	WHOLE PULP	14 MESH FRACTION	28 MESH FRACTION	48 MESH FRACTION
BREAKING LOAD, G	17.5	18.9	17.8	13.4
CROSS-SECTIONAL AREA, μM^2	164	186	147	172
BREAKING STRESS, KG/MM^2	117	107	123	94
MODULUS, KG/MM^2	1355	1120	1175	1040



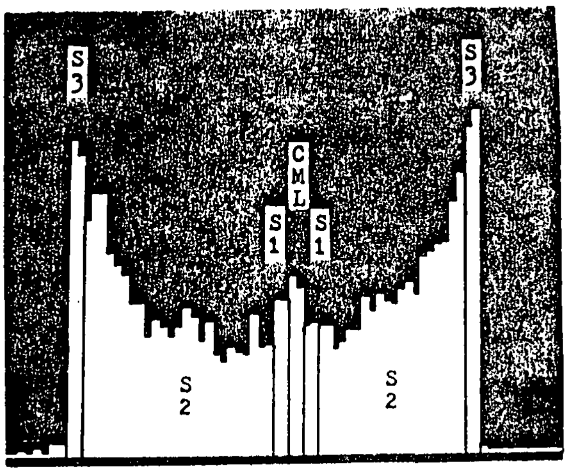
Effects of chemical treatments and refining on tensile strength of SCMP.



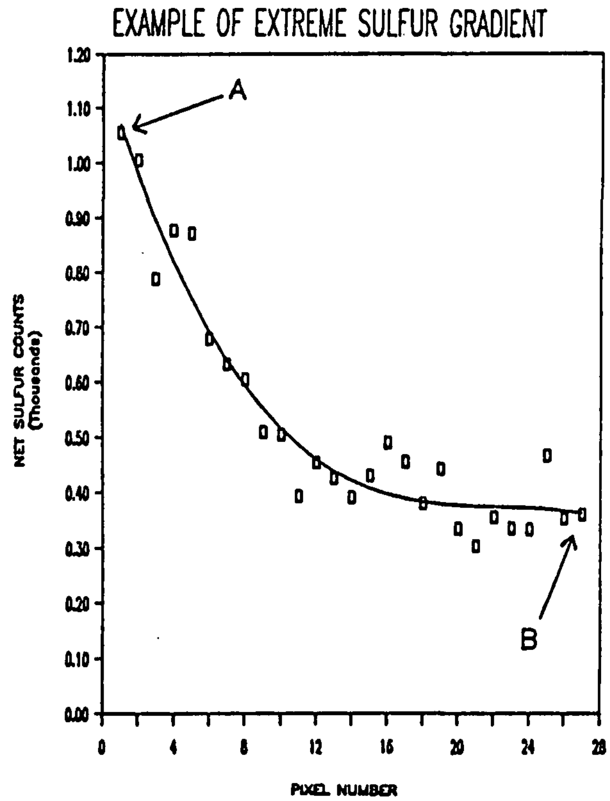
Effects of pressing, press-drying, and refining on tensile strength of untreated and ozone treated SCMP.

RELEVANT STUDENT RESEARCH

T. HEAZEL	PH.D. 1987
T. CORNBOWER	M.S. 1987
H. DUNDORE	M.S. 1987



Extreme example of wet sulfur count histogram from double-wall linescans.

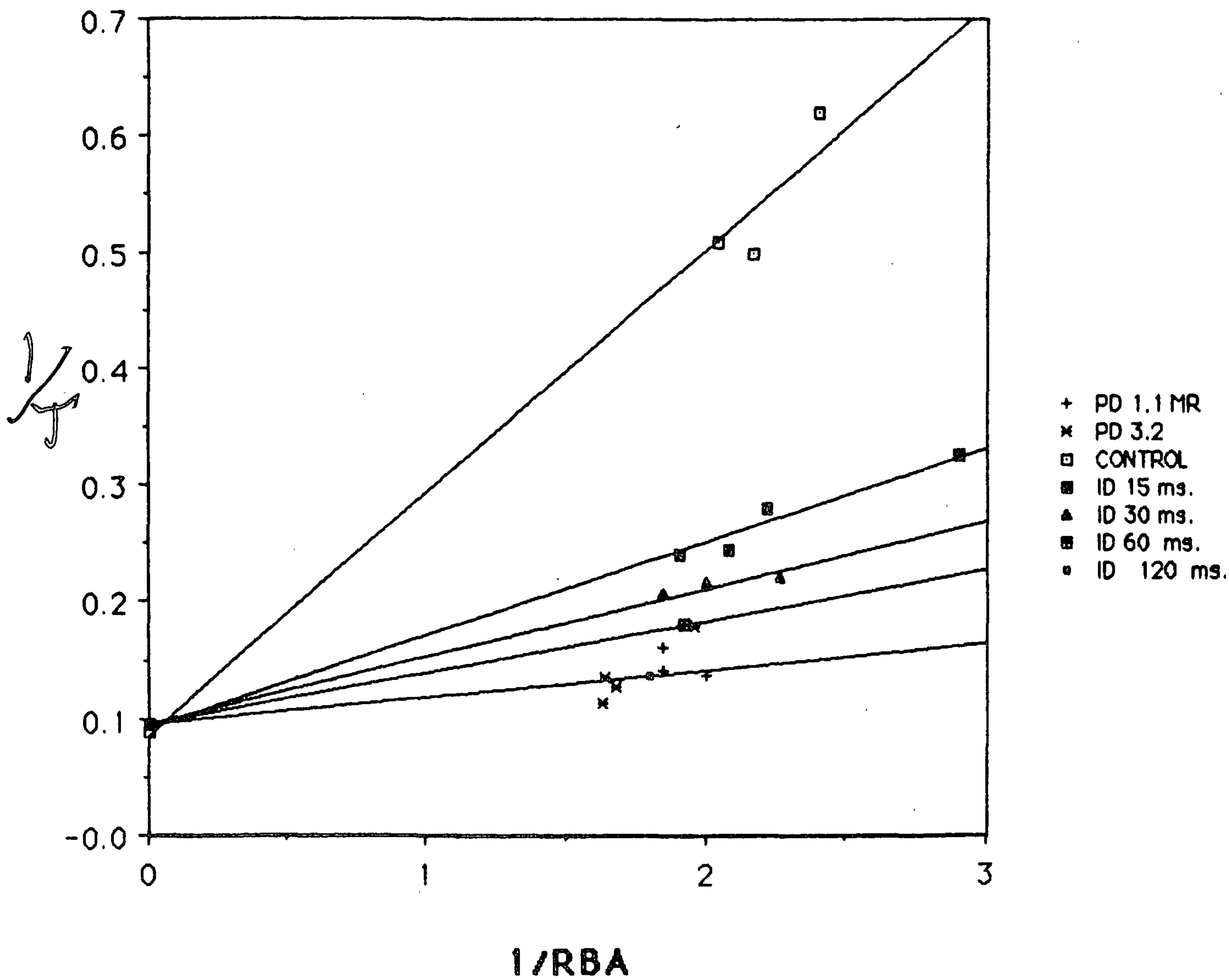


Smoothed linescan wall as single secondary wall.

Time, min	Na_2SO_3 Concentration, g/L liquor	Net Sulfur Counts[a] A	B	CC	A/B	CC/B	S
20	60	288	188	530	1.65	2.97	225
20	130	393	262	773	1.49	2.89	304
20	200	672	398	1177	1.70	3.01	474
40	60	270	185	537	1.59	3.18	212
40	130	433	277	799	1.68	2.84	343
40	200	913	640	1733	1.42	3.08	722
Mean ± 95% conf. int.:					1.59 ± 0.15	2.98 ± 0.22	

[a] A = maximum near lumen; B = minimum in S2; CC = cell corner; S = mean secondary wall (S_2 + S_3)

Treatment means for various parameters used to describe the degree of sulfonation of different cell wall layers.



Page equation plots for press-dried and impulse dried SCMP.

SIMULATED THERMOMECHANICAL PULPING
OF HYDROLYZED CHIPS

	Hydrolyzed Chips		Control Chips	
Lignin, %	29.7	31.0	30.0	29.7
Xylan, %	5.1	4.6	9.8	10.0
Mannan, %	10.4	10.3	16.2	16.2
C.S.F.	89	105	111	106
PFI Rev.	1140	985	1750	1730
Density, g/cc	0.60	0.58	0.46	0.46
Burst Index, $KPam^7/g$	2.26	2.13	1.34	1.20
Tensile Index, N·m/g	48.7	44.0	34.4	33.7
Tear Index, $mN \cdot m^2/g$	4.42	5.06	3.51	3.26

DIRECTIONS

- Bonding strong fibers
- Effects of refining variables on fiber strength retention
- Failure mechanisms
- Fiber modification

Evening Session

Earl Malcolm

PRELIMINARY IPC RESEARCH BUDGETS (1987-1988) - CHEMICAL SCIENCES DIVISION ($1000)

IPC FUNDED

Chemical Pulping	
3288 - Fine Structure of Wood Pulp Fibers	70
3475 - Fundamentals of Selectivity in Pulping and Bleaching	150
3474 - Improved Processes for Bleached Pulp	60
3477*- Development and Application of Analytical Techniques	13
	293
Recovery	
3473-1-Fundamental Processes in Alkali Recovery Furnaces	250
3456-2-Smelt-Water Explosions	20
3477* -Development and Application of Analytical Techniques	13
New -Computer Model of Recovery Furnace	40
	323
High Yield Pulping	
3566 - Separation of Strong, Intact Fibers	175
3524 - Fundamentals of Brightness Stability	140
3521-2-Raman Microprobe Investigation of Molecular Structure and Organization in the Native State of Woody Tissue	45
3477*- Development and Application of Analytical Techniques	13
	373
Other	
3534 - Exploratory Research	60
3477*- Analytical (Paper)	21
	81
TOTAL IPC FUNDED	1,070

PRELIMINARY IPC RESEARCH BUDGETS (1987-1988) - CHEMICAL SCIENCES DIVISION ($1000)

CONTRACT RESEARCH

Government Funded		
3473-6-Fundamental Studies of Black Liquor Combustion		
	IPC	230
	NBS	135
3521-3-Raman Microprobe Investigation of Molecular Structure and Organization in the Native State of Woody Tissue		102
		467
Nongovernment Funded		
River Survey		200
Other		100
FKBG		50
Analytical Services		200
		550
	TOTAL CONTRACT RESEARCH	1,017

TOTAL FUNDED AND CONTRACT-- 2,087 (49% Contract)
(51% IPC Funded)

PRELIMINARY IPC RESEARCH BUDGETS (1987-1988) - CHEMICAL SCIENCES DIVISION ($1000)
IPC FUNDED

Chemical Pulping

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